UCL
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Centre for Sustainable Heritage

Doctoral Thesis

Lifetime of Colour Photographs in Mixed Archival Collections

by

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in collaboration with The National Archives

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To my family.

I, Ann Fenech, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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Abstract

Chromogenic prints, which make up around 99% of all colour photographs, are amongst the most vulnerable materials in archival storage. However, although environmental standards for storage are available, antagonistic requirements within archives mean that the recommended conditions are not always appropriate. This study evaluated the impact of mixed archival storage on chromogenic prints by following three lines of research: environmental, material and values.

During storage, three environmental parameters predominantly influence chromogenic print lifetime: temperature, relative humidity (RH) and pollutants. The pollutant of greatest interest was determined to be acetic acid as it is the most abundant pollutant within archival boxes and also causes greatest changes in dye concentrations.

Materials research focussed on the development of two non-destructive analytical methods. The first used the sRGB colour model for monitoring dye concentrations. The second combined near infrared spectroscopy to develop applications for dating and stability prediction of chromogenic prints.

The third line of research related to values, specifically fitness-for-purpose of an image within the context of an archival collection. A psychophysical approach was taken to determine the point at which colour changes are no longer acceptable, defined as the unacceptability threshold. It was identified that while assessor characteristics did not affect the threshold, image characteristics, particularly fading profile and image detail, did.

Having investigated the three lines of research separately, their integration led to a more holistic approach. Accelerated degradation experiments were planned using design-of-experiment principles to develop a multiparametric dose-response function. The function relates the rate of degradation to temperature, RH and acetic acid concentration. This allowed for isoperms and isochrones, which connect

points of equal permanence and lifetime respectively, to be developed.

Finally, an innovative photographic lifetime calculator has been developed using principles of stock modelling and the developed damage function, thus incorporating material and value change dependent upon environmental parameters.

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List of Definitions

ΔE_{RGB} A single number that represents the normalised difference between two colours in the sRGB colour model.

damage function Function of unacceptable change to objects dependent upon agents of deterioration and time.

dose-response function Function of change in physical properties (of an object) dependent upon agents of deterioration and time.

end-of-lifetime The point in time until which the value present in an object survives.

informational value Value associated with objects due to written or recorded information.

isochrone A curve connecting points of 'constant lifetime'.

isoperm A curve connecting points of 'constant permanence'.

lifetime Period of time during which a photograph retains its value.

mixed archival collection A mixed archival collection in this project refers to a collection where different types of materials are stored together. Therefore, colour photographs are found in the same archival boxes as paper, amongst other materials.

photographic lifetime calculator A computational stock modelling tool that incorporates a damage function that allows collection managers to assess the effect of different environmental scenarios on the lifetime of chromogenic prints in their collection.

Photographic Preservation Index The "preservation quality" of an environment at the time of measurement, compared to 20 ℃ and 50% RH, fo photographic materials..

Unacceptability Threshold The ΔE_{RGB} classified as unacceptable by users of colour photographs.

List of Symbols and Abbreviations

AA Acetic acid.

ANOVA Analysis of Variance.

B&W Black and White.

BS British standard.

CCD Central Composite Design.

CMY Cyan Magenta Yellow.

CSH-HSL Centre for Sustainable Heritage, Heritage Science Laboratory.

DAD Diode Array Detector.

DMSO dimethylsulfoxide.

DOE Design of Experiments.

FIA Flow injection analysis.

HPLC High Performance Liquid Chromatography.

ISO International Standard Organisation.

JND Just Noticeable Difference.

MVA Multivariate Analysis.

NIR Near Infrared.

NO Nitrogen monoxide.

NO_2 Nitrogen dioxide.

NO_x Nitrogen oxides.

O_3 Ozone.

OBA Optical brightening agent.

PI Preservation Index.

PLS Partial Least Squares.

ppb parts per billion.

PPI Photographic Preservation Index.

pzc point of zero charge.

RC resin-coated.

RGB Red Green Blue.

RH Relative Humidity.

RMSECV Root Mean Square Error of Cross Validation.

RMSEP Root Mean Square Error of Prediction.

SNV Standard Normal Variate.

SO_2 Sulfur dioxide.

STEL Exposure Limit.

T Temperature.

TFA Trifluoroacetic acid.

TNA The National Archives.

tVOC total Volatile Organic Compounds.

TWA Time Weighted Average.

UT Unacceptability Threshold.

VOC Volatile organic compounds.

WWII World War II.

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Chapter 1

Scope of Work

1.1 Introduction

Chromogenic colour photography was introduced by Eastman Kodak in 1935 when Kodachrome film appeared on the market. This was followed by Agfa's Agfacolor film in 1936 and by the Ektachrome films in 1940, a new product from Eastman Kodak [1]. Chromogenic colour prints soon followed as direct positives in 1941 and via the negative process in 1942, both developed by Eastman Kodak [2].

Chromogenic prints now represent more than 99% of all colour photographic prints in existence [3]. However, due to technical limitations in the development process, the number of dyes that can be incorporated is limited and most are inherently unstable. Therefore, in comparison with other heritage materials, chromogenic prints are very vulnerable to change [2].

We are now at a crucial moment in the history of classical photography because digital photography has gained ground while traditional photography has declined. As a result, technical knowledge within research departments of the photographic companies is being lost due to changes in the industry. This knowledge is, however, essential for museums and archives as it relates directly to the specific preservation requirements of the materials in their collections, and to their permanence. Hence, as colour photographs are found in most mixed material collections, it is essential that effort is invested in lifetime studies of photographs [4]. This PhD study attempts to make a contribution to this effort.

Because photographs are chemically and physically more complex than most archival materials, some basic understanding of how they are made and how they

age is essential to their proper care [5]. Appropriate standards of preservation are especially important since, unlike black-and-white (B&W) photographs, the stability of chromogenic prints is not achieved primarily by the processing method. Rather, it is the storage conditions that will predominantly affect the lifetime of chromogenic prints [6]. Dyes found in chromogenic prints are known to be particularly sensitive to unfavourable environmental conditions [7]. Therefore, it is essential to understand the conditions in the storage environment.

In many collections, photographs are often stored in folders and boxes with other materials. Despite the number of published standards for long-term storage of photographs, environmental conditions in archives are normally set to suit the most abundant archival material, i.e. paper, rather than the colder and drier storage conditions necessary for colour photographs [8]. Hence, it is of great importance to understand how the environmental conditions provided in such mixed archival collection storage environments affect the lifetime of colour photographs.

In this project, 'lifetime' is defined as the period of time before which an object becomes unacceptable with respect to its primary value, i.e. until its value has been consumed. In this case, utility value, specifically informational value, was considered to be the value of interest as it is the information held within the images that is of greatest importance to archival users, including of The National Archives (TNA), Kew [9, 10][1]. The present study was carried out in collaboration with TNA and its collection used as a case study for this project.

This PhD study considers three main lines of research that influence the lifetime of chromogenic prints: conditions of storage (environmental research), dye degradation (material research) and perceived utility of the objects (value research). It investigates how these three areas relate to each other. A photographic lifetime calculator has been developed to incorporate material and value change dependent upon environmental parameters. Using this lifetime calculator collection managers are able to assess the extent of change under different environmental management scenarios. This makes optimal management of collections of chromogenic prints in mixed archival collections possible.

[1] TNA is the official archive of the UK government and holds 900 years of documentary history with records ranging from parchment and paper scrolls through to digital files and archived websites [10].

1.2 Research Questions

The following research questions are addressed in this study:

- What is the impact of storing chromogenic prints in mixed archival collection on their lifetime?
- What are the principal degradation factors in the storage environment to these materials?
- How do these degradation factors affect the lifetime[2] of these prints?
- Can the stability of these prints be characterised in a rapid and non-destructive manner?
- How can the point of functional loss, or end-of-lifetime, be assessed?
- What factors affect the utility value of these prints in archival storage?
- Can the environmental conditions of storage, the material stability, and value aspects be integrated together into a single model?

1.3 Aims and Objectives

The main aim of the research is to evaluate the impact of storage in mixed archival collections on colour photographs. To reach this aim, the following objectives have been set:

- To create a research collection of chromogenic prints for the testing and experimental phases of the study.
- To investigate the micro and macro-environmental conditions present in archival storage.
- To develop a non-destructive method to characterise the stability of dyes in chromogenic prints.

[2]Lifetime: period of time during which a photograph retains its utility value.

- To determine the relationship between the utility value of a photograph and dye degradation and, therefore, determine the end of lifetime for a colour photograph.
- To devise and implement an experimental design plan for accelerated degradation of colour photographs.
- To construct a multiparametric dose-response function for lifetime prediction of prints dependent upon environmental parameters.
- To integrate the multiparametric damage function into a photographic lifetime calculator to serve as an options appraisal tool for collection managers.
- To survey colour photographs in The National Archives' collection as a means of testing the photographic lifetime calculator.

1.4 Thesis Organisation

This thesis is divided into eight chapters. In the first chapter, an overview of the research is given. Chapter 2 then gives a brief insight into the development of colour photographs to set the context for why such materials are unstable.

Chapters 3-5 develop the three lines of research - environmental, material and value - further. Each chapter starts with an introduction to the field of research, and follows on with the work done for this project within that area. Chapter 3 describes why environmental conditions are of relevance to the lifetime of chromogenic prints, together with a study of the environmental conditions present in mixed archives, as exemplified by TNA. Chapter 4 discusses the necessity of non-destructive methodologies in the heritage field, together with the non-destructive methods developed for the purposes of this research. Chapter 5 concludes this set of chapters with a discussion on values and heritage research, together with a description of the methodology developed and implemented for the assessment of lifetime of chromogenic prints.

Chapters 6 and 7 link the three lines of research together. Chapter 6 describes the accelerated degradation experiments carried out to determine the effect of environmental conditions (temperature, relative humidity, and pollutants) on chromogenic prints. Then, Chapter 7 discusses the photographic lifetime calculator developed for assessing environmental scenarios for the preservation of chromogenic prints in

mixed archival collections. The National Archives are used as a case study for this lifetime calculator.

Chapter 8 concludes the work by identifying the main conclusions and innovations of the work as well as suggestions for further studies.

Chapter 2

Colour Photography & the Chromogenic Print

As introduced in Chapter 1, this PhD project looks at modelling the lifetime of chromogenic prints by integrating three lines of research. These three lines of research - environmental, material and value - will be discussed in chapters 3-5. However, it is essential to first understand the nature of colour photography and, specifically, chromogenic prints.

This chapter provides a brief description of the development of colour photographs prior to chromogenic prints. This helps to put their development into context, particularly why they became so ubiquitous given their inherent instability. After discussing the chromogenic print in more depth, the final section then introduces us to the research collection developed as part of this project.

2.1 Brief History of Colour Photography

Chemical photography saw its start in the 1820s with Nicéphore Niépce. At first, photography was solely a B&W technique. This was primarily due to limitations of innovation. At the time, some photographers were also quite prejudiced against the aesthetic properties of colour photographs. In fact, some considered B&W to be the 'true' form of the medium, as evidenced by Roland Barthes' observation in 'Camera Lucida'[1] that colour was "applied...to the original truth of the black and

[1] One of the most influential studies on the criticism and theorisation of photography, published in 1981.

white photograph" [11].

Of course, this was not a universally-held principle. It was also widely appreciated that colour in photography would allow for the representation of images as we see them. Hence, there was also a movement for the production of a colour photograph.

2.1.1 Capturing Colour Images

In the first instance, the most straightforward remedy for producing coloured photographs was to hand-tint monochrome photographs to give the illusion of a colour print [12]. However, this is not colour photography as we understand it today.

The first record of the production of colours on a silver chloride coated paper was by Sir John Frederick William Herschel in 1840. However, he found problems with fixing and retaining these colours, rendering the process ineffective [12]. Thus, the search for inherent rather than applied colour continued. Numerous technologies were developed (Figure 2.1). However, very few had commercial success.

2.1.1.1 Additive Processes

The first permanent colour photograph was produced by James Clerk Maxwell in 1861. It was obtained by first producing three black and white negatives, each shot through a red, green or a blue filter. Three black and white glass positives were then prepared from these negatives and the images were projected through three magic lantern projectors[2] fitted with the corresponding red, green and blue filters used in the original negatives and superimposed (Figure 2.2).

The process used by Maxwell was an additive process as beams of red, green and blue light were merged to reproduce an image. Besides this triple-projection method, there have been three major additive methods used in photography:

- Successive frame method - B&W images of the same scene are obtained through filters of the three colours and, then, the image is remerged by projecting these same three images back through the same three filters and superimposing the projected images at a rate that is too fast to be seen.

[2]Early type of image projector.

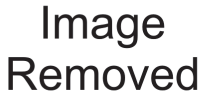


Figure 2.1: Tree structure describing colour photographic processes. It identifies chromogenic prints as an indirect subtractive multilayer process [13].

Figure 2.2: The superimposed image of the first permanent colour photograph: A tartan ribbon and rosette [14].

- Lenticular method - image is obtained on a furrowed film (surface with 'bumps') and emulsion[3] at the other end so that the image is focussed on different points.
- Mosaic method - a filter composed of specks of the three colours is used to obtain the first image and, then, this image is projected through the same filter [15].

The successive frame method has been used mainly in cinematography and television but never successfully in print photography. Similar may be said for the lenticular method, which had only limited applicability in print photography. The mosaic method was the most successful additive method due largely to the success of the autochrome plate (section 2.1.2).

2.1.1.2 Subtractive Processes

By the start of the 1930s the limitations of the additive processes, though representing more than 300 different patented processes, were becoming very much apparent. New research efforts were invested in the subtractive process-based technology.

In subtractive processes, the process is focussed on the light that is reflected/ transmitted, rather than depending on light absorption as in the additive process (and, thus, limiting the light passing through). The dyes absorb the constituents of one of the primary colours in the white light spectrum and transmit the other two [16, 17]. The image is, thus, obtained through the colours complementary to the red, green and blue (RGB) used in additive processes i.e. cyan, magenta, and yellow (CMY).

[3]As in most cases in photography, although called an emulsion, chemically it is a dispersion.

All light falling on the photographic emulsion is captured by one layer or another. This method of direct recording allowed for more natural colours to be achieved with chromogenic development materials [2]. It also eliminated the need of taking the emulsions apart as is often required with the horizontal organisation typical of additive systems [18]. Hence, subtractive colour photography formed the basis of twentieth-century colour photography.

2.1.2 Commercial Processes

The first colour processes were developed in the 1890s [19] with the first commercially available colour photographic process being the autochrome. The autochrome was the first fully practical colour plate, becoming available around the beginning of the 20^{th} century. It used dyed potato starch grains measuring 0.01-0.02 mm in diameter, interspersed with carbon black to fill gaps. These were underlain by a gelatine-bromide emulsion (Figure 2.3). It was registered by Louis Jean Lumière and his brother Auguste Marie Nicolas Lumière on December 17, 1903 as French patent no. 339,223.

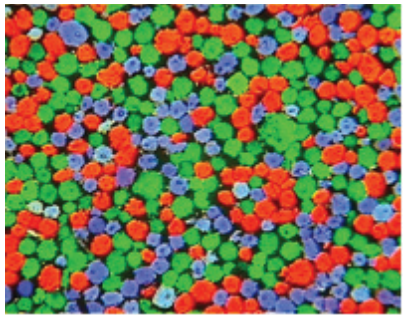


Figure 2.3: Photomicrograph of a Lumière plate with the silver layer removed (x200) [20].

Although patented in France in 1903, it was only patented in the US (patent no. 822,532) in 1906. It became commercially viable from 1907 and was around till 1932 [12]. For these 25 years, it was the most popular and available colour process on the market [12]. Other mosaic methods, such as the Finlay and Thames (1906) and Dufaycolor (1908), also had commercial success. However, they were not infinitely reproducible, being made from a single exposure on glass, as opposed to the roll-film negatives in use for monochrome photography at the time. This problem was only solved with the introduction of chromogenic photography.

2.1.2.1 Chromogenic Colour Photographs

As discussed in Section 1.1, chromogenic photography was introduced in 1935 with the Kodachrome[4] film. Kodacolor[5], the first negative-positive print, was introduced in January 1942 [2, 21].

Kodacolor was the first colour-negative roll film from which colour prints could be made [12] and the first consumer-oriented mass production negative-positive colour print process [21]. Then, in 1946, Kodak Ektachrome was put on the market. This was the first colour film that could be developed by the photographer rather than returned to the factory for processing, giving the photographer more control of the final product. With these developments, colour photography became widely available to the amateur photographer. By the 1960s, colour photography had become the most widespread photographic medium overtaking the B&W amateur photofinishing market in the US [21].

2.2 The Chromogenic Print

Chromogenic prints are generally composed of a base on which a light-sensitive emulsion is coated. The term 'chromogenic' originates from the way in which the colour (chromatic) dyes are generated during the development process, where developing agents produce coloured products on oxidation [22].

The basic principles of the chromogenic photographic system are intimately linked with the nature of the human eye. Just as the retina is sensitive to red, blue and green light, so the colour photograph is composed of three emulsion layers approximately corresponding to the sensitivity of the visual receptors. The dyes in each sensitive layer are, then, of the complementary colour to the light the layer absorbs (Figure 2.4). So, the red-sensitive layer forms a cyan dye, the green sensitive layer a magenta dye and the blue sensitive layer a yellow dye.

This section discusses the main components of chromogenic prints, i.e. the support as well as the image. Particularly, it focusses on negative-positive chromogenic prints as they are the focus of this work. A brief overview of these components is shown in Figure 2.5.

[4]The suffix 'chrome' usually indicates a transparency or print made via the reversal process (where a positive image is obtained directly).

[5]The suffix 'color' usually indicates a colour negative or print paper.

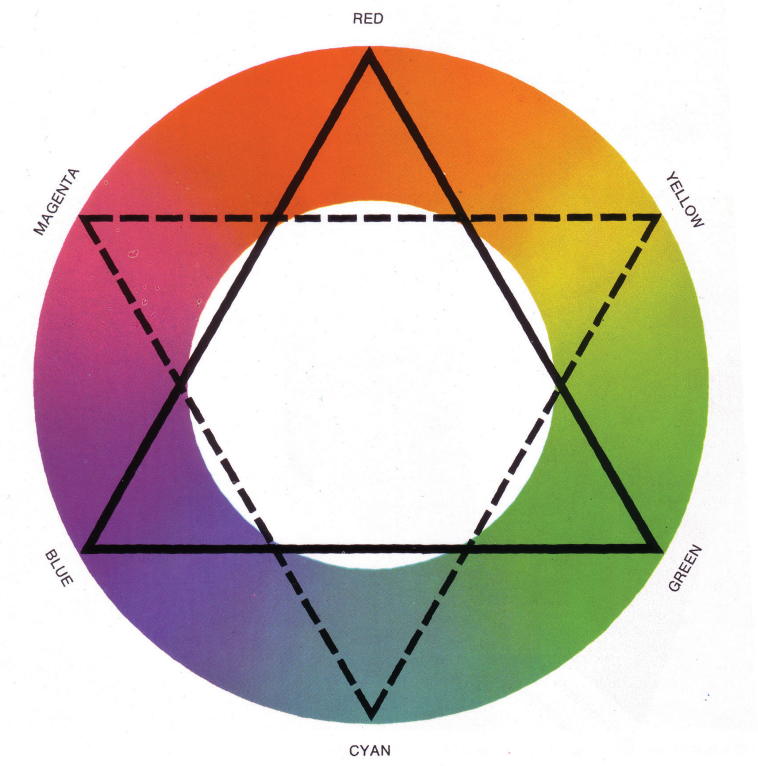


Figure 2.4: The relationship of colours used in photography. The solid line represents the three colours to which the emulsion layers are sensitive while the opposite points on the dashed-line triangle represent the complementary colour of the dyes [23].

2.2.1 Photographic Print Supports

Throughout the years, five predominant supports have been used in photographic materials: metal, glass, plastic film and paper, though some more unusual processes have used ceramics, leather or cloth [1, 24, 25]. However, without a doubt, paper remains the predominant support for prints. The development of photographic paper made sensitive to light using silver salts (developing-out paper), as well as printing-out paper (paper that produces a visible image on direct exposure) has been attributed to a number of inventors, including Hellot in 1737, Carl Wilhelm Scheele in 1777, and Thomas Wedgwood and Humphry Davy in 1802 according to different sources [26–28].

In terms of commercial products, Eastman Kodak introduced the Eastman Negative Paper in 1884. This, initially, rag paper was changed into 50% rag fibres/50%

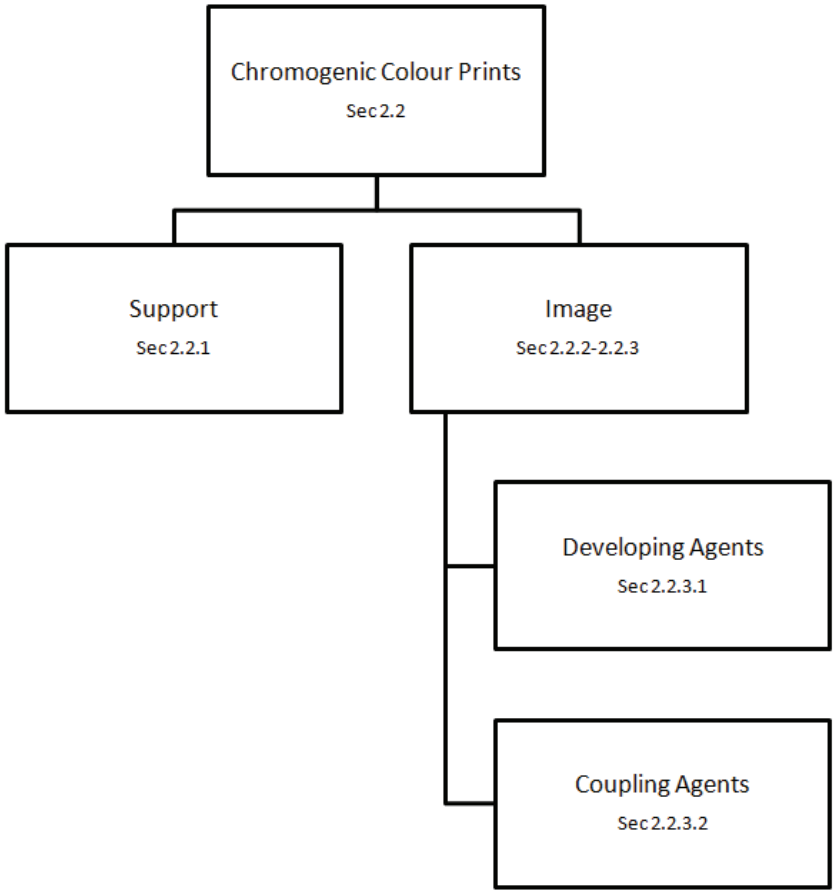


Figure 2.5: The main components of a chromogenic photographic image and the relevant sections where they are discussed.

purified wood cellulose fibres in 1926 and then, 100% highly purified cellulose fibre in 1929. During this time, stearate-sizing also replaced rosin sizing[6] [27]. Nevertheless, today, alpha cellulose is the main component of photographic paper with standards stating that beta and gamma cellulose must make up less than 4% [29].

The most common types of photographic paper supports are baryta-coated paper and resin-coated (RC) paper, with RC paper the most common contemporary base [24, 29]. However, there is a smaller choice for colour than for B&W printing papers, with no fibre-based papers available for colour prints and, generally, a narrower range of contrasts[7] being available [30]. Today, by far the most common substrate

[6]Size is a material added to change the properties of the paper, such as absorption characteristics.

[7]Contrast is a measure of the difference between tones that can be produced on the paper. Mid-tones tend to be undifferentiated in very low contrast papers while there may be no mid-tones

for colour prints is RC paper [30].

2.2.1.1 Baryta Paper

Baryta paper, also called fibre-based paper, was introduced in the photographic industry in about 1885 and is still used to this day for high-quality B&W photography [29]. It is composed of a paper base covered with an emulsion of barium sulfate (baryta) in a gelatine binder on top of which a light-sensitive emulsion (generally of silver halide grains in gelatine) is coated (Figure 2.6); contemporary practice, however, makes use of titanium dioxide instead of barium sulfate [24]. Typically, these papers were manufactured in both single weight and double weight with a few extra heavy 300 g/m^2 base papers being manufactured for the fine art print market [31].

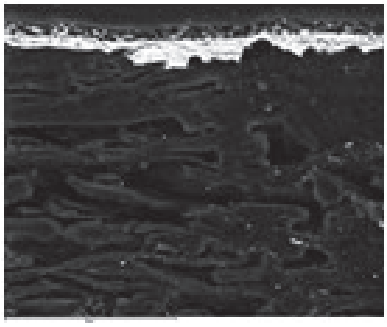


Figure 2.6: The backscatter environmental scanning electron microscope image of a cross-section of modern fibre-based, B&W photographic paper. The image clearly shows the baryta layer (white) between the paper base and the emulsion layer (courtesy of the Getty Conservation Institute)[32].

The baryta layer is added to a photographic base for a number of reasons. First of all, it covers irregularities of the fibre-based paper surface, thus giving a very smooth overcoat. This improves the brightness of the base as its reflective capacity is improved and extends the tonal range of the highlights, giving superb image quality [29, 31, 33, 34]. Optical brightening agents (OBAs) are also sometimes added to improve the optical whiteness of the paper, a practice that started in the 1950s [29]. Furthermore, this layer prevents the transfer of paper impurities to the image, as well as the absorption of processing chemicals by the paper base through

in very high contrast papers.

the light-sensitive emulsion [24, 33]. Another advantage is that the resultant paper has high durability [31].

While precise manufacturing details remain trade secrets[8] - and are, moreover, prone to frequent changes - experience has shown that photographic paper may be superior in terms of stability to most other types of paper i.e. paper used for other functions, such as writing paper. This is possibly due to the high alpha-cellulose content, freedom from aggressive chemicals and special sizing agents that give photographic paper excellent wet strength [1].

Nevertheless, there are also a number of disadvantages, the main one being that the thick emulsion layer, the baryta layer and the paper base all absorb large quantities of processing chemicals. Their washing out and drying prolong the process and require large volumes of chemicals. Hence, the last baryta chromogenic photographic paper, besides for alternative printing processes, Agfacolor mcnIII, disappeared in the mid-1970s. This paved the way for RC paper [29].

2.2.1.2 Resin-Coated Paper

During WWII, the military tried to perfect a photographic paper that required a shorter processing regime [29, 35]. This was done by coating the paper with a hot melt of a cellulose derivative, similar to that used in film, making the photographic paper impermeable to solutions. This was, however, expensive, as was coating paper with a solvent solution of cellulose acetate, a process used after WWII [35].

Then, in the second half of the 20^{th} century, the photographic industry started to look for a way of how the photographic process could be sped up, essentially making it cheaper. Due to the affinity of water for hydroxyl groups available for hydrogen bonding in the paper, a system of preventing water accessibility to the fibre base was required [27, 35]. This research eventually gave rise to the first B&W RC (or PE, polyethylene) photographic papers in the early 1960s, with Kodak introducing the first RC colour photographic paper in 1968 [31, 35–37]. These RC papers quickly replaced the fibre-based papers used previously [38].

[8] A list of additives to Kodak's raw base in 1945 contained: muriatic acid (pH adjustment), melamine-formaldehyde (wet strength agent), aluminium chloride, stearic acid/NaOH (produces sodium stearate, and mixes with $AlCl_3$ to make aluminium stearate, which acts as an internal size providing increased water resistance), gelatine tub size (external gelatine size that can provide wet strength if hardened and generally acts as a surface sizing agent), blue dye used in most paper, magenta dye used in about 5% of papers, corn starch (dry strength), beater gelatine (dry strength) [21].

RC papers consist of a resin coated paper base that consists of a mid-weight paper (typically 180 g/m^2) laminated on both sides with a thin layer of polyethylene. The side of the light-sensitive emulsion is then coated with pigments to make it opaque (Figure 2.7). A modern polyethylene-coated paper has a thickness of around 250 μm and a weight of approximately 270 g/m^2 [39].

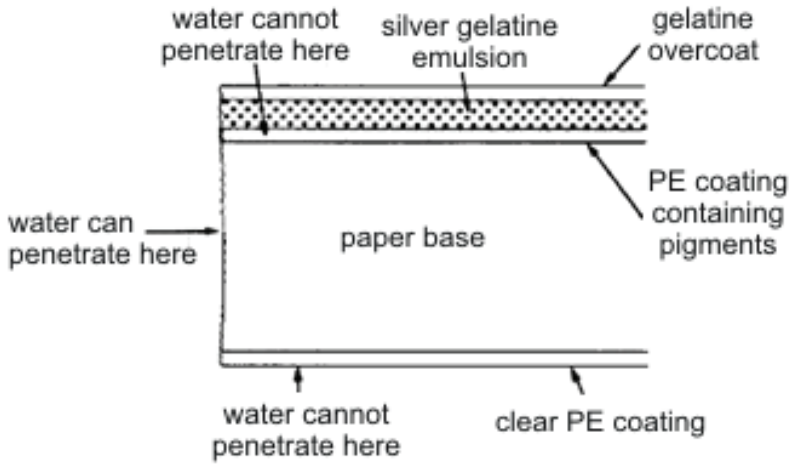


Figure 2.7: Schematic cross-section of a RC paper [1].

The polyethylene layer is generally composed of a mixture of low-density and high-density polyethylene, or high-purity layers of one of these [40]. Polyethylene was chosen due to its availability and thermal stability, thus making it ideal for photographic paper. Also, it can be used easily as a coating by extrusion[9], is chemically inert to most solvents and chemicals, and is impermeable to water while remaining flexible [35].

Due to the resin coating, washing agents do not penetrate into the paper structure as much as with previous paper supports. This minimises the volume of washing solution required, as well as the drying time, hence speeding up the process. Also, a super-coat is added onto the gelatine emulsion to help protect it from abrasions during development, which would produce black marks, and an anti-static coating is added [33, 35]. Moreover, these papers keep their rigidity when wet and have good mechanical resistance, allowing for mechanisation of the process and, hence, very rapid processing in roller transport machines [29, 31, 39]. Thus, they represent the

[9]A high-volume manufacturing process in which a softened material is forced into a mould to produce an object with a continuous profile.

colour photographic papers used in around 99.5% of all colour photographs today (with some sources claiming that all colour papers are RC papers) [39, 41, 42].

Furthermore, since these printing papers are reflection prints, the light passes through the dye deposits twice rather than once (though some of the light is lost through absorption by the support). This allows for thinner imaging layers and, thus, less silver and dye coupler[10] [42]. However, due to this thin polyethylene layer, barium sulfate is not adequate; a pigment with a higher refractive index is required as this provides greater sharpness and reflective whiteness in the images particularly in areas of highlight [35]. Titanium dioxide (TiO_2) started to be added to the raw base of RC supports around 1984 [21]. It is used either on its own or with zinc oxide [31].

There is an ongoing debate about the archival qualities of RC papers. Some research suggests that plastic resins emit gases that in time cause the emulsion to degrade, while others state that the resins used for photographic papers are stable [41]. However, if no resin coating is applied, it is very probable that, on developing the photographic papers, the cotton fibres become soaked in fixing chemicals. These can themselves, in time, degrade the emulsion, and at a faster rate than the gases emitted from the resin coating [41].

Besides the possible emission of reactive gases from the resin-coating, these photographs have also displayed a number of other problems with stability. One of the earliest problems was cracking of the polyethylene layer on the face-side of glass-framed photographs on exhibition [29]. This was found to be the result of a photo-chemical oxidation reaction of the polyethylene layer. These reactions were mitigated by introducing anti-oxidants in the paper base [1]. Also, some prints have a yellowish border, rarely more than a few millimetres, on the back of the prints, caused by penetration of the processing solutions between the two plastic layers, from where the chemicals are practically impossible to remove [29].

Furthermore, the titanium dioxide added to pigment the polyethylene layer on the face (image) side is also photoactive. It leads to the production of singlet oxygen when exposed to light, which can react with polyethylene, resulting in chain scission and, thus, rigidity and cracking of the layer as it expands and contracts with the emulsion layer. It can also react with the dyes [29, 31]. To reduce light induced

[10] A chemical that reacts with the developer to produce one of the colours in a print or transparency.

oxidation of the RC support catalysed by TiO_2, a stabiliser has been added, either in the face-sided polyethylene layer, or in the paper core to help absorb these oxygen radicals [21, 31]. Nevertheless, it seems that RC paper prints are more susceptible to oxidising pollutants than baryta paper prints, possibly due to the impermeability of the base layer, thus limiting its absorption capacity for oxidation products or pollutants to limit degradation [31].

Also important, at least for some papers, are design constraints. These include a lower hardening level to increase the development rate, the use of gelatine substitutes to reduce water-load and to reduce curl, and higher levels of emulsion stabilisation to reduce the risk of staining in high-temperature processes [31]. In fact, RC papers cannot be heat-glazed, though they get a gloss finish, as many have been found to react negatively to heat [30, 39].

As with baryta paper, the detailed compositions of these supports are not known for most time periods. However, it is known that in 1988 the layers and additives of Kodak RC colour prints were as follows: emulsion layers (CMY), pigmented PE layer (TiO_2, zinc oxide, optical brightening agent - OBA, magenta dye), raw base (paper fibre, antioxidants, TiO_2, OBA), backprinting, clear PE layer, antistatic layer (colloidal silica) [21]. Nevertheless, some additives may not be listed, and the composition would have changed over time including the specific composition of each additive. All this results in a complex material that has constantly changed in composition.

2.2.2 Development of Chromogenic Images

2.2.2.1 Formation of the Latent Image

Photographic images are captured by projecting an image onto a light-sensitive material. This is generally an 'emulsion' of silver halides in a film of gelatine (though albumen and collodion were used in the past and synthetic polymers are also used). When light falls on the silver halide grains, imperfections in the crystal (a perfect crystal is not a good photon absorber) cause the grain to absorb photons leading to the reactions:

$$Ag^+Br^-(\text{crystal}) + h\nu(\text{radiation}) \rightarrow Ag^+ + Br + e^-$$
$$Ag^+ + e^- \rightarrow Ag^0 \text{ (to a small extent forming small silver clusters)}$$

The latent image that forms is a result of the increased sensitivity of silver ions to reduction due to the already present small clusters of silver [18, 43]. Thus, the fundamental basis of photography is based on the influence of light on photosensitive silver halide crystals [44].

The choice of silver halide is based on the fact that the formation energy of interstitial silver ions through crystal imperfections is in the order of AgCl > AgBr > AgI, while the activation energy of the migration of interstitial silver ions is in the reverse order as a result of the difference in ionic characters [45]. Hence, silver bromide is the most commonly used halide, with chlorides used for slow development and iodide for some faster development for films. Nevertheless, most photographic papers generally contain some silver chloride as the light-sensitive material [18, 46].

Silver halide grains are naturally sensitive to blue light. Other colour sensitive layers need spectral sensitisers. Spectral sensitisers, discovered by Hermann Wilhelm Vogel in 1873, absorb light in a specific range of the spectrum, thus extending the range of absorption in which silver grains can be excited [47]. The presence of colour sensitisers is also required for the vertical organisation of a photographic film or paper (Figure 2.8) [18].

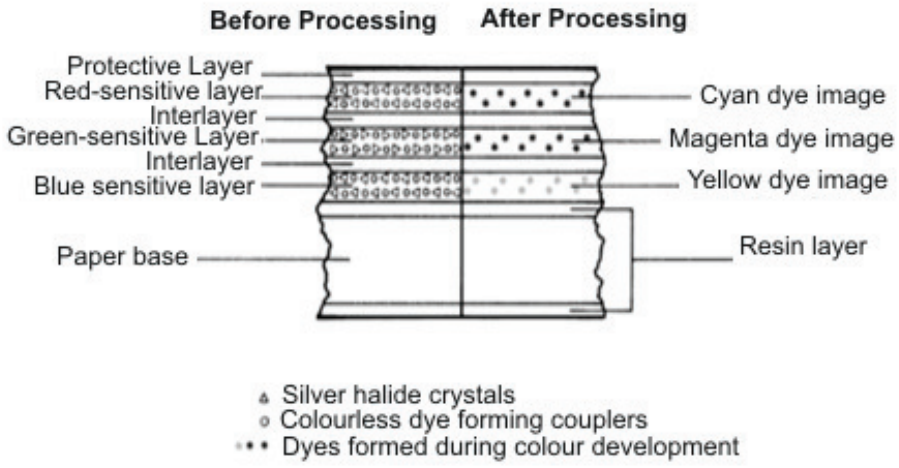


Figure 2.8: Cross-sectional diagram of a contemporary colour paper on resin-coated paper base [42].

The conventional emulsion dye layer order is (top to bottom) yellow, magenta and cyan. Light passes through the blue-sensitive (yellow-dye producing) layer first, then the green-sensitive (magenta) layer, and finally the red-sensitive (cyan) layer

[21]. Due to the sensitivity of silver halide grains to blue light, a yellow filter may be placed between the top blue-sensitive layer in an emulsion and the lower layers to limit the blue light passing through to the lower layers [18].

This is, however, not required for photographic paper used to produce positives from negatives due to the illuminants used when developing the negative film [18]. In fact, when the Kodacolor negative-positive system was introduced in 1942, both the film and paper were arranged in the conventional layer order. However, in 1954, the dye layer order for negative working prints was reversed (Figure 2.9) [21]. This arrangement provides smooth, mottle-free images, in spite of the comparatively rough surface of the extruded polyethylene layer. This occurs due to the low visual contrast of the yellow image with the white support [42]. This remains in use today in all negative-working print materials [21].

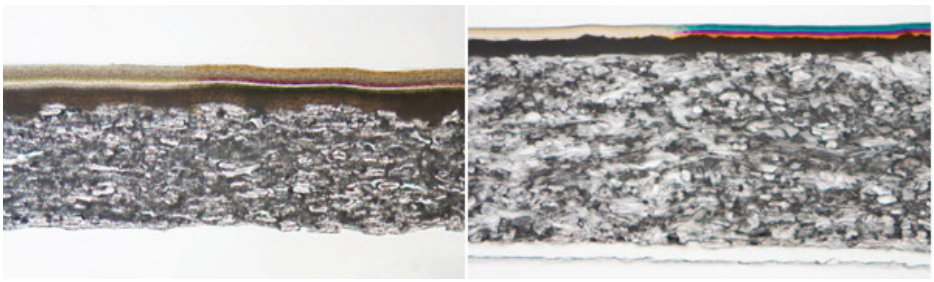


Figure 2.9: Kodacolor (1947) paper (left) showing the conventional emulsion layer order and Supra Endura (2008) paper (right) showing the reversed emulsion layer order in a contemporary negative-working paper [21].

2.2.2.2 Dye Formation

In chromogenic processes, dye formation can take place during development of the image in the areas of exposed silver via one of three possible pathways [15, 48]:

- Primary colour development: dyes are formed by the oxidising action of the exposed silver halide on the developing agent.
- Autocoupling colour development: an oxidised developing agent forms the dye by coupling with itself or with its reduced form.
- Secondary colour development: oxidised developing agent reacts with a coupler.

Of these three colour development possibilities, primary colour development and autocoupling have not found practical use due to various limitations particularly in the control of colour development. Also, the dyes and the precursors have similar dimensions, but while the precursors need to penetrate into the film, the dyes should remain where they are [49]. Thus, secondary coupling development, where colour photographic images form as a result of the reaction between the oxidised developing agent and organic dye precursor molecules known as couplers, is the development process of choice [18].

Probably the first reference to the use of an oxidised developing agent to produce colour dyes was by Benno Homolka [50] when in 1906 he used a coloured organic compound to investigate the oxidising nature of the latent image [21]. However, it was his collaborator, Rudolf Fischer, who realised the potential of this method to produce colour photographic processes. Fischer coined the phrases 'colour developer' and 'colour formers' (dye couplers) in a patent filed in 1912. Then, he further explained the process of chromogenic negative-positive photography followed by a list of colour developers and dye couplers in 1914 [21, 51, 52].

Secondary Coupling Development Process

The secondary coupling development process is a complex one, not least due to the complex nature of the oxidised colour developer [53]. The first step is a two-electron oxidation process of the *p*-phenylenediamine (1), a developing agent (Figures 2.10), by silver halide, via a semiquinone (2) (Figure 2.10-2.11) to give a quinonediimine (3) (Figure 2.11). Then, the semiquinone, being highly reactive and unstable (though its lifetime is prolonged by resonance), is itself completely oxidised [54]. This oxidation can occur either via a homogeneous dismutation[11] of two molecules of semiquinone to give *p*-phenylenediamine (1) and a quinonediimine (3) (Figure 2.11) or by a heterogeneous reaction with the latent image silver halide to give a quinonediimine (3) (Figure 2.11) [17, 53].

The quinonediimine is the compound that reacts with the coupler, since it is a more powerful electrophile than semiquinone diimine. The coupler is deprotonated to give an anionic structure, which, together with the quinonediimine, forms the leuco dye, or a substituted leuco dye (Figure 2.12) [17].

[11] A reaction between two molecules where one is oxidised and one is reduced.

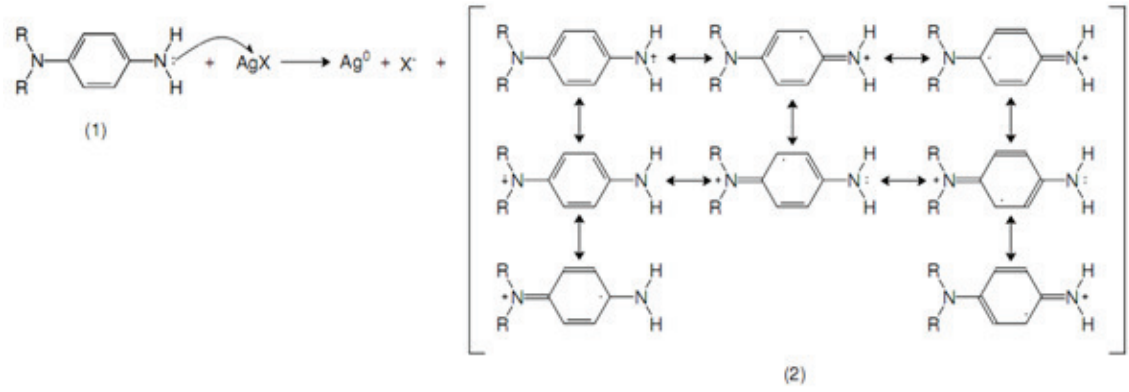


Figure 2.10: First oxidation step of the developing agent: Oxidation to the semiquinone [17]. (1) *p*-phenylenediamine, a developing agent; (2) semiquinone.

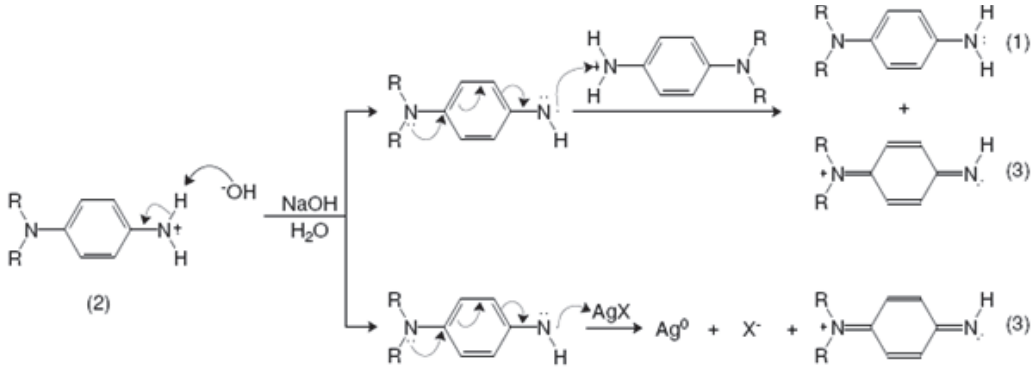


Figure 2.11: Second oxidation step of the developing agent: Oxidation of the semiquinone to the quinonediimine [17]. (1) *p*-phenylenediamine, a developing agent; (2) semiquinone; (3) quinonediimine.

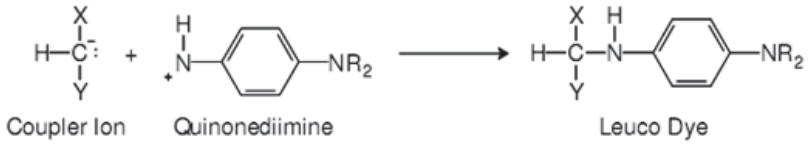


Figure 2.12: Production of the leuco dye [15].

The next step is the double oxidation of the leuco dye to produce the coloured dye (Figure 2.13). This can be done by atmospheric oxygen, silver ions, or oxidised forms of the developing agent [3]. However, oxidation by air would not explain the existent ratios of colour development to light exposure. Also, the dye is not always produced close enough to any silver grains (this can be explained by the quinonediimine being

deaminated in the alkaline solution giving quinine monoamine that is stable enough to diffuse and being reformed by reacting with excess developing agent, Figure 2.14) [46]. Thus, the probability is that the oxidising agent is the oxidised developing agent (quinonediimine) [17, 46].

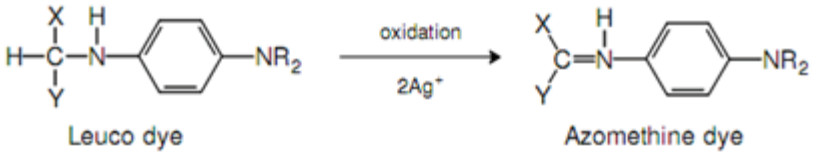


Figure 2.13: Oxidation of a leuco dye to an azomethine dye [15].

Figure 2.14: Deamination of quinonediimine in alkaline solution [46, 55].

However, many competing reactions may occur with the quinonediimine giving a number of unwanted products [17]. These side reactions, which tend to lead to the formation of dimers or, at least, to diminished brilliance of the dye image, are the result of low coupling and dye formation rates.

The secondary coupling development process was confirmed from kinetic spectroscopic data, which followed the evidence from quantum-mechanical calculations, by the linear combination of atomic orbitals - molecular orbitals method [46, 56]. This method, which supposes that molecular orbitals can be constructed from the linear superposition of atomic orbitals centred on individual atoms, is one of the most common assumptions used to determine molecular structure in computational chemistry.

2.2.2.3 Post Development Processing

Following dye formation, the unexposed silver halide needs to be removed from the photographic paper since, otherwise, this would darken over time. This process is known as fixing. The chemical most commonly used is sodium thiosulfate, which forms a coordination compound with the unexposed silver to form a soluble complex [17].

$$AgBr + S_2O_3^{2-} \rightarrow AgS_2O_3^- + Br^- \text{ (adsorption complex)}$$
$$AgS_2O_3^- + S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} \text{ (desorbed)}$$

However, the silver image, which has now carried out its function of producing the dyes required to form the image also needs to be removed. Thus, this silver is converted back to silver halide prior to the fixing stage with the use of a bleaching agent, such as [Fe(III)EDTA] [17]. The two stages are often known jointly by the term 'blix'. The last step is always followed by rinsing to wash away any remaining soluble by-products.

Often, a colour negative is first obtained, which is converted to a colour positive by re-photographing the colour negative and carrying out the same process outlined above[12] (Figure 2.15). In these negative-positive products, a masking dye is also used to filter out unwanted light during printing. The orange masking agent used today in colour-negative films explains the orange colour of these same negatives [58].

2.2.3 Photographic Dye Components

Photographic dyes are chemically complex compounds formed during the development process. Thus, prior to understanding photographic dye degradation, it is important to understand the components making up a dye, and how different substituents on these components help improve (or otherwise) the resultant dye.

The main components of a dye are colour couplers, which are embedded in the different emulsion layers to produce the required dye in that layer; the developing agent, which is added in the form of a developing solution to effect the conversion of the latent image into a dye image; as well as other components added to the structure to facilitate the process, such as ballasting groups used to 'anchor' the colour couplers (and the resulting dyes) in the required emulsion layer. All components making up a dye - coupler, ballasting groups and developing agent - come together to determine the final composition and nature of the dye [4].

For a coloured compound to be considered as a dye, an auxochromic group with an 'excitable electron' has to be present in the structure [53]. Organic compounds are known to be intensely coloured if they contain a polymethine structural unit (having

[12]The overall process, when starting from green light reflected off an object is: green light from scene→magenta dye in negative→yellow and cyan dyes in print→green light reflected from print [57].

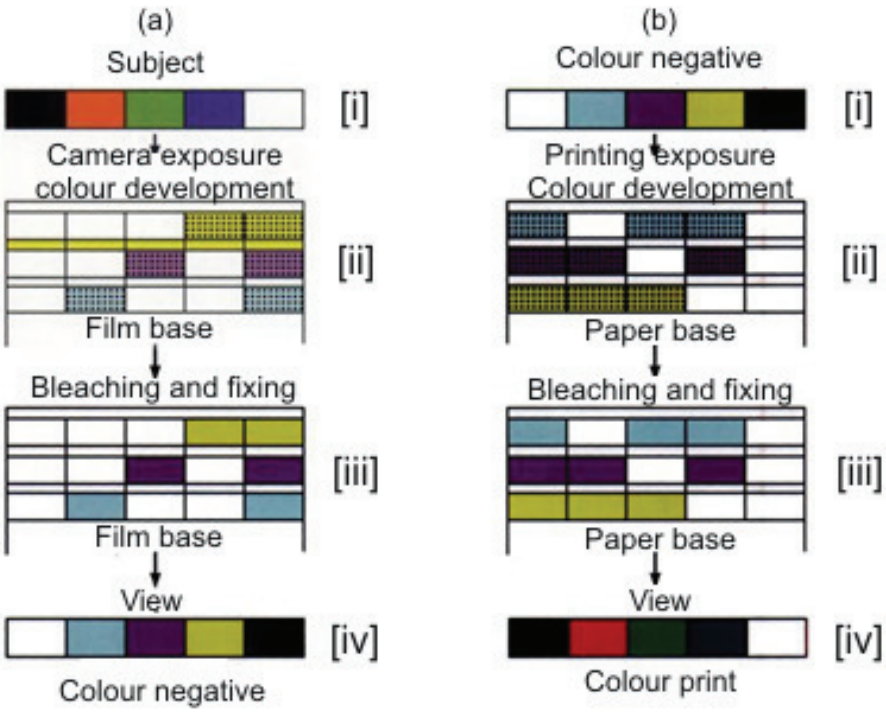


Figure 2.15: The colour negative-positive process [39]. [a.i] Original subject represented by patches of colour; [a.ii] Cross section of colour negative film after the silver halide grains exposed in the camera have been developed to produce negative silver images and dye; [a.iii] Cross section of colour negative film after the silver grains have been bleached out; [a.iv/b.i] Colour negative viewed by transmitted light; [b.ii] Cross section of colour paper after the silver halide grains have been developed to produce silver and dye images; [b.iii] Cross section of colour paper after the silver images have been bleached, leaving only the positive dye images; [b.iv] Dye images formed in the colour print as they appear when the print is viewed by reflected light.

an odd number of methine groups (-CH=) bound together by alternating single and double bonds) or any other unsaturated conjugated system, as recognised by König in 1926 [56]. Then, this was extended to cover free radicals with a polymethine structural unit. Aromatic compounds and polyenes have also been found to produce intense colours, if sufficiently large to result in conjugation, since all contain π-electrons [56]. Thus, it was these classes of compounds that were investigated for colour production in photographs.

2.2.3.1 Developing Agents

For a compound to be appropriate as a developing agent, there are a number of properties that it must possess. These include:

- Reductive properties towards the exposed silver grains to the exclusion of unexposed grains,
- Stable to other oxidation processes, especially aerial oxidation,
- Producing dyes with good colour stability and quality,
- Sufficiently soluble in water or alkaline solutions (to be satisfactorily soluble in the developing solution),
- Producing colourless, soluble oxidation products,
- Non-toxic and safe [48, 49, 59].

Ideally, one developing agent should be capable of producing all the dyes required.

It was Rudolf Fischer who demonstrated how couplers may be used to form dyes by the secondary colour development process using only one colour developer [48, 49, 52, 53]. He showed that when developing agents of the *p*-phenylenediamine or *p*-aminophenol type react with compounds containing one of these three main groups:

(i) Compounds with an active open-chain methylene (-CH_2-) group,

(ii) Compounds with an active cyclic methylene group,

(iii) Phenolic compounds (and naphthols) with an active methine (-CH=) group [46, 48, 49, 60],

a condensation reaction results that could produce indamine, indophenol, indoaniline or azomethine dyes (Figure 2.16). All of these compounds have extensive conjugated systems, making them coloured [15, 49]. Since indophenols tend to be sensitive to even slight changes of pH and indamine production reactions are quite slow, modern dye-forming colour photographic processes rely on indoanilines and azomethines [15]. Yellow couplers are usually in group (i), magenta in groups (i) and (ii), and cyan couplers in group (iii). Thus, magenta and yellow dyes tend to be of the azomethine

family (being produced from an active methylene compound) and cyan dyes are generally indoanilines (produced from a phenol) [15, 46, 49, 60].

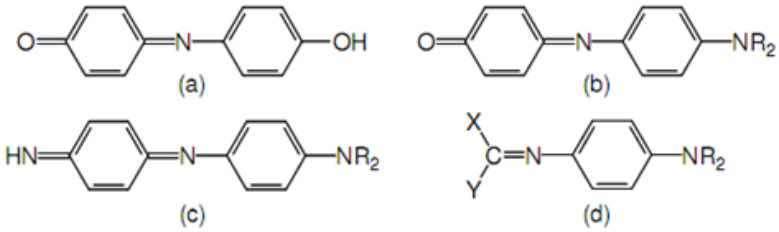


Figure 2.16: The basic structure of the four types of dyes as proposed by Fischer: (a) indophenols; (b) indoanilines; (c) indamines; (d) azomethine [15, 49].

Although *p*-aminophenol had also been suggested as a developing agent by Fischer, it is only *p*-phenylenediamine derivatives that can form the indoaniline and azomethine dyes. Also, though *p*-phenylenediamine has been around as a developing agent since 1888, in its non-substituted form, it is a very weak developing agent particularly due to its slow speed of action [49]. Thus, it is virtually only its derivatives that have found practical use [17, 48, 61]. As coupling occurs at a free amino group (NH_2), this free amino group must be retained in derivatives [15].

Derivatives in which both the hydrogen atoms of one of the amino groups are replaced by alkyl groups, such as dimethyl-*p*-phenylenediamine, are generally much more active than the unsubstituted *p*-phenylenediamine [15, 46, 49]. Also, since the developing agent needs to be capable of donating electrons to silver ions, often an alkyl group is added to the ortho- position of the benzene ring relative to the coupling amino group to facilitate this donation and speed up the process [15, 49].

A problem with the resultant compounds is that they tend to have irritant properties. Thus, one of the groups on the substituted amino group is generally modified to minimise this effect (Figure 2.17). Substituent groups effective in reducing the allergenic properties of this compound, probably by limiting skin penetration, are the sulfonamido and carbonamido groups [15, 61, 62]. Since these compounds are very sensitive to aerial oxidation, they tend to be produced as salts or complexes, which are more stable [15].

Although the original developing agent was *p*-phenylenediamine, the only two colour developer compounds that have survived, CD-3 and CD-4 (Figure 2.18), are really toluenediamines and not *p*-phenylenediamines. Both are used in the industrial

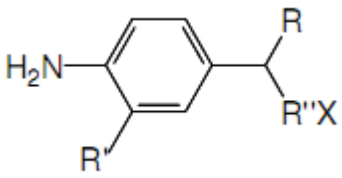


Figure 2.17: General structure of a developing agent (R, R' = alkyl group; R" = alkylene group bearing the substituent X, where X is a substituent on the amino group that makes the developing agent less prone to causing dermatitis and other skin problems, such as the sulfonamido and carbonamido group. The two forms represent the resonance system [49].

standard processes C-41[13], E-6[14] and RA-4[15] depending on requirements. CD-4 has better developing power for silver halide and is, thus, used when photographic speed and high development efficiency are required. On the other hand, CD-3 gives more brilliant colours, which also exhibit greater stability to fading. Thus, CD-4 is commonly used for chromogenic negative films while CD-3 is used for chromogenic prints [53].

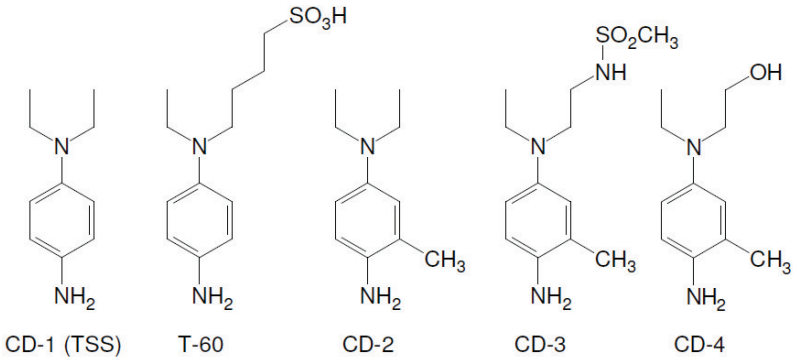


Figure 2.18: Colour developers. TSS (CD-1) and T-60 were used in Agfa's older colour process papers, which were not compatible with the standard processes. CD-2 was a colour developer, which was previously used. CD-3 and CD-4 are the colour developers used in the industrial standard processes [17, 53, 63].

[13]Chromogenic colour print film developing process.
[14]Chromogenic colour reversal (slide) developing process.
[15]Chromogenic colour print developing process.

2.2.3.2 Coupling Agents

In secondary colour development, dyes form as the developing agent reacts with couplers giving magenta, yellow or cyan dyes depending on the coupler structure [15, 46, 49]. Despite their diversity, couplers may be represented by the formula ZCHXY, where Y and Z represent parts of a chain or ring structure while X represents a hydrogen or a leaving group (Figure 2.19) [17, 64].

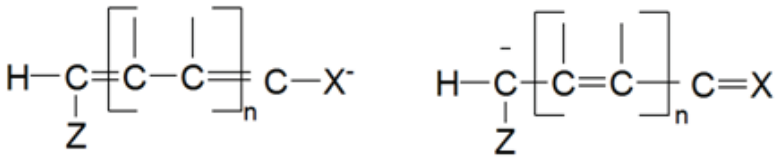


Figure 2.19: General structure of a coupler where X represents an electron-attracting atom or group e.g. O or N, Z is an unsaturated grouping that may (or may not) be joined to the carbon-bearing X (as indicated by the dotted lines) and n is 0 or 1 [49].

The couplers may either be added during development or incorporated into the gelatine layers; incorporation can either be carried out by adding long-chain molecules to the couplers to make them immobile (Agfacolor principle) or by suspending the dye couplers in microscopically small droplets of an oily substance (Kodacolor or Ektachrome principle, also known as the substansive system) [1, 15, 42, 49].

Until the early 1950s when more stable paper was introduced, the incorporated couplers resulted in a lower dark stability. However, this is no longer an issue [65]. In fact, the Kodacolor principle, using suspended dye couplers, remains the main chromogenic development system nowadays [1]. The average particle size of most coupler dispersions for use in photographic coatings is approximately 0.05-0.1 μm [53].

There are a number of different couplers in use as the photographic companies continuously strive for improvement. Amongst the properties that are important for a coupler are:

- High rate of reaction: required for the production of sharp images,
- Good solubility,
- Low proneness to migration,

- Colour purity,
- High coupling activity,
- High extinction,
- High sensitivity and low fog[16],
- Good emulsion stability,
- Low granularity,
- Availability and price,
- The solubility of the dye formed,
- The stability of the dye formed,
- The colour of the dye formed [15, 40].

However, compromises are often needed.

Although the exact structure of the couplers has changed over time, the typical class of a specific coupler has tended to be more or less uniform especially due to the streamlining of processes between different companies. The most important yellow-forming couplers are α-pivaloylacetanilides and α-benzoylacetanilides; the most important magenta-forming couplers are 5-pyrazolinones, indazolones, pyrazolobenzimidazoles and pyrazolotriazoles while cyan couplers tend to be substituted phenol or naphthol-type couplers [4, 17].

Yellow-Forming Couplers

As has already been stated, yellow couplers tend to contain an active open-chain methylene group with the general formula X-CH_2-Y, where X=RCO and Y=R'CO or R'NHCO. The couplers react with the developing agent by replacing the two hydrogen atoms (Figure 2.20) [15]. The resultant yellow dyes tend to be of the azomethine class having an absorption maximum preferably between 430 and 460 nm. The most important characteristics for yellow couplers tend to be tinctorial strength and dye

[16]If the development process is continued for a sufficiently long time, all the silver halide, including the unexposed, will be converted to silver. This unselective development is referred to as fog [46].

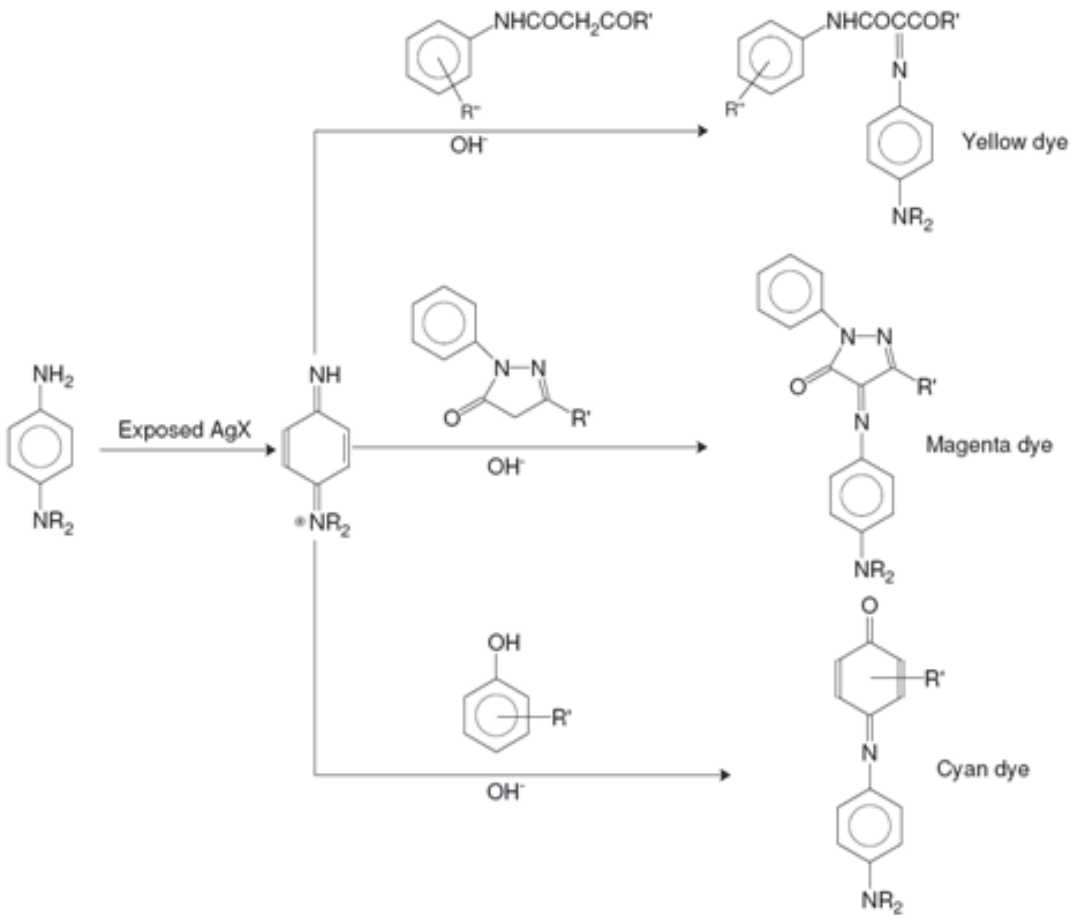


Figure 2.20: General coupling reactions [65].

yield; for good colour reproducibility it is essential that the absorption spectrum of the resultant yellow dye has a sharp-cut curve[17] in the long-wavelength side [53, 66].

Yellow-forming couplers are generally acylacetamides, specifically acylacetarylides and especially anilides, with some hetarylides (aliphatic amides produce azomethine chromophores with a much lower tinctorial strength than anilides and slower coupling rates and are, thus, not widely used) [15, 53]. Of these, α-pivaloylacetanilide and α-benzoylacetanilide classes are the most common; α-pivaloylacetanilide generally produces dyes with better light stability and narrower bandwidths while benzoylacetanilide couplers often produce dyes with higher colour density due to the higher extinction coefficients of the dyes [17, 53]. Others, such as indazolones and benzisoxazolones, have also been reported [17].

[17]This means that the absorption of the yellow dye immediately decreases.

Magenta-Forming Couplers

Over the years, most magenta couplers have been heteroaromatic compounds with absorption maxima at 530-580 nm and with very few, if any, open-chained compounds. Also, until 1980, magenta couplers were generally pyrazolones. Exceptions were Agfa colour paper MCN, where an indazolone magenta was used, and Agfachrome CT-13 reversal films, where a combination of pyrazolone and pyrazolo[1,5-a]benzimidazole type couplers were in use; these couplers were chosen by Agfa for their brilliant hues [67]. Today, although the absolute predominance of heterocyclic compounds remains, the predominance of pyrazolone-type magenta couplers has decreased [67, 68].

Until recently, the 5-pyrazolinone-type couplers have been most extensively used. Gradually, 3-arylamino- and 3-acylamino- substituted compounds have also been introduced into colour film and colour paper particularly with the introduction of standardised processes based on CD-3 and CD-4 (namely C-41, E-6, and RA-4). In these cases, generally, the couplers have a ballasting group attached to the 3-position [17, 67].

Also, pyrazolotriazoles, particularly pyrazolo[5,1-c](1,2,4)triazoles, have been introduced in colour negative paper where their low reactivity does not affect the end result due to their improved thermal stability and less intense unwanted absorptions, especially regarding the side absorption at 440 nm; this absorption was found to be negligible though present. Nevertheless, the characteristics of pyrazolo[5,1-c](1,2,4)triazoles did not correspond to the needs of the industry mainly due to their comparatively low coupling activity, high aggregation tendency and poor light stability of the resulting azomethine dyes. However, pyrazolo[5,1-b](1,2,4)triazoles have now become the main class of magenta couplers for colour paper and colour film [67].

Other compounds have also been mentioned in the literature as capable of producing magenta dyes and have been used in the industry with variable levels of success. These include enamine type couplers and indazolones, which were withdrawn from use when it was determined that the resultant brilliant dyes produced were unstable to actinic light[18] as well as sensitive to photochemical damage [67].

[18]Light that affects photographic film or paper.

Cyan-Forming Couplers

Virtually, all cyan couplers are either substituted phenol or naphthol type couplers (or at least heterocyclic) with ballasting groups attached to the 3-position of the amide group. The dyes from the early cyan couplers had a problem with stability, but, as with the other couplers, substitutions of key groups brought about major improvements in the stability, colorimetric properties and yield of the resultant dyes. In particular, 2-aryl-5-(acrylamido)phenols have been mentioned for their superior hue and dye stability [17]. Since these couplers are weak acids ionising in alkaline solutions, the reactions with the developing agent occurs at the 4-position [67].

2.3 The Research Collection

Colour photographs in archival collections, including those at The National Archives (TNA) are valuable objects that cannot be sampled or destroyed for the purpose of materials research. Thus, it was essential that a research collection on which this research could be carried out was assembled at the start of the project.

2.3.1 Methodology

Chromogenic negative-positive colour photographic prints are predominant in most archival as well as private collections, and they form the materials in the research collection. Other technologies are not represented.

Chromogenic (negative-positive) prints were collected from a wide variety of sources, mainly by donation from friends and colleagues or purchased, particularly to cover the earlier years. Once received, each item was given a reference number and details including source, country of production, manufacturer, backprinting present, and date of development were noted if known. The objects were then stored at 4 °C.

2.3.2 Results and Discussion

The research collection contains over 1,000 items. The collection covers the whole period of production of chromogenic photographs, from 1942 to the present (Figure 2.21). As expected, the earlier products were the hardest to find and include within the research collection. Prints from the 1970s and onwards are best represented

within the collection. This coincides well with the developing dominance of the colour market over the B&W market.

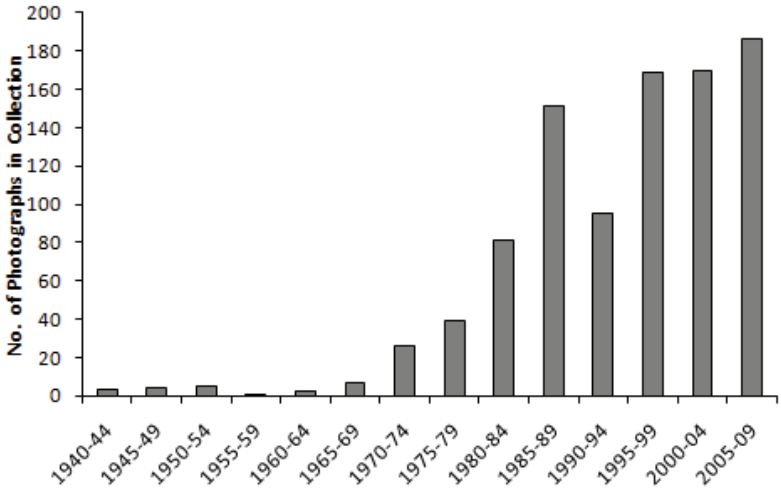


Figure 2.21: Frequency plot for year of production for the research collection materials for objects with known date of development.

However, date of development is not the only material variable. Efforts were made for the research collection to cover a variety of countries of production (including UK, India, US, Malta, Slovenia, Slovakia and Denmark) and manufacturers (Figure 2.22). Also, both fibre-based materials (mainly pre-1970s) and resin-coated materials (post 1970s) are included within the research collection.

As might be expected when developing such a collection, it is not possible to cover every single print type. In particular, smaller companies and print classes have not all been included e.g. only one print by Mitsubishi is included. Also, most of the earlier prints (pre-1960s) are Kodak prints. However, Kodak was not the only chromogenic print manufacturer at the time. In fact, Agfa put its first chromogenic printing material, Printon, on the market in 1945 [69]. However, these early Agfa products are not easily found. Nevertheless, as in the early years Agfa products were not widely available outside Germany [1], these materials are not expected to be found within archival collections in the UK to a wide extent. In particular, no chromogenic colour prints pre-dating the 1960s were found within TNA's collection during a search through the archives. Hence, this was not considered to be a major deficiency of the research collection in light of the current project.

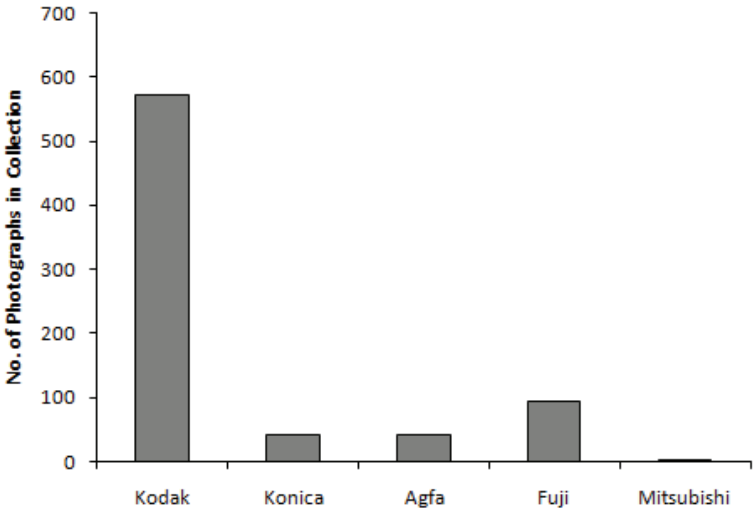


Figure 2.22: Frequency plot for manufacturers represented in the research collection materials for objects for which this information was known.

2.4 Conclusion

Colour photographs represent a wide-ranging set of materials produced using a number of different technologies. Nevertheless, the vast majority of colour photographic prints found in archival (as well as private) collections are chromogenic negative-positive photographic prints printed on baryta paper (pre-1970s) or RC paper (post-1970s).

Chromogenic prints were developed to fill the gap in the market for an easy-to-develop, reproducible and cheap colour photographic print. This focus means that such prints are amongst the most vulnerable materials found within archival collections. To understand this vulnerability, it is essential to understand their material chemistry and stability.

Due to the high quality of paper, the supports used in photographic prints are generally more stable than papers used for other purposes (and more so than the plastic supports used for films) [24, 29]. Having such a stable support, the major vulnerability of these materials lies with the image.

As has been shown in Sections 2.2.2 and 2.2.3, formation of the image is a complex process. Due to a variety of requirements regarding the development process, a very limited array of chemical compounds have been used. Also, stability was typically not a top priority for the manufacturers.

Ideally, a study of the stability of these materials would include knowledge of each individual component in each photographic print present within a collection. This would allow for an analytical prediction of stability of the image based on its chemistry. Unfortunately, this is not feasible in the current circumstances as most details of manufacture remain trade secrets [21], with most (if any) of the information publicly available being available within patent documents [53]. However, patents do not reveal if any of the compounds have been put into commercial use, and, more importantly, in which photographic papers they have been used.

A solution to this issue could potentially be the use of reference compounds for the development of mock-up materials. However, just as the information available about the materials is limited, so is the availability of these compounds. This problem has been made even more acute as most photographic manufacturers are severely limiting, if not closing down, their research and development departments within this field. Thus, most of the knowledge is being lost as scientists have either retired or moved on as the industry shifts rapidly towards digital (Figure 2.23) [4, 70, 71].

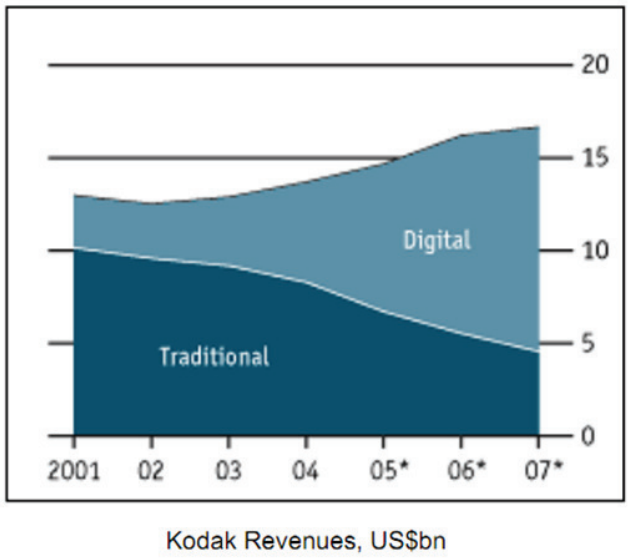


Figure 2.23: Kodak's revenue balance between the digital and the traditional sectors between 2001 and 2007 showing the rapid decline of the traditional sector and the concurrent increase within the digital sector [71].

Nevertheless, though very little is known about exact compositions that can lead to the development of relevant mock-ups, as has been discussed in this chapter, the

production reactions of these materials are generally well-known. It is also known that the material changed relatively quickly as manufacturing companies strived to improve some of the numerous aspects of their materials. These changes came in useful in the materials research, as did the fact that though the dyes are complex, a limited amount were used in each single print.

For these reasons, the most practical solution was the development of a research collection that represented as closely as possible the vast majority of photographic material present in practice, as discussed in Section 2.3. This research collection served as the basis for research carried out in the following chapters.

Chapter 3

Environmental Research

This chapter outlines why the storage environment is of prime relevance to the lifetime of chromogenic prints (Section 3.1). Then, the discussion focusses on the environmental factors of significance, namely temperature and relative humidity (Section 3.2), and pollutants (Section 3.3).

As temperature (T) and relative humidity (RH) are continuously monitored at TNA (Section 3.2.4), particular effort was invested in monitoring pollutant concentrations, as discussed in Section 3.3. The results obtained show which environmental parameters are of greatest concern and provide the context for the investigations explored in the subsequent chapters.

3.1 Colour Photographs & their Storage Environment

Based on the current state of technical knowledge, very few, if any, colour photographs can be described as permanent. This is particularly true for chromogenic prints [6]. Indeed, Kodak, in a 'Handbook for the Professional Photographer', stated that "colour papers contain dyes which are as stable as possible, consistent with other requirements. Like other dyes, they may change in time"[72]. Thus, due to their chemical composition and physical nature, chromogenic prints - particularly the images - are fragile records that require suitable conditions for long-term preservation [6, 73].

Material stability depends on the interaction of a variety of factors. It is not

only influenced by material structure but it also depends on its interactions with the physical, chemical and biological components of its environment. These can induce changes in both the composition and the structure [74]. Stability of photographic materials, in fact, relies on three main factors:

- Material composition and structure,
- Processing and post-processing methods,
- Manner of storage and use [58].

Normally, not much, if any, influence can be exerted on the composition and processing methods of photographs that are found within archives, as public records are not selected on the basis of their material composition [6]. Records at TNA are selected with the aim of preserving the 'national memory' by documenting government decision-making, activities and processes from the official records of the United Kingdom Government and other records as specified in the first schedule of the Public Records Act 1958 (as amended) [75].

Therefore, it is only the methods of storage and use that can be controlled to ensure the long-term stability of photographs [76]. This is particularly relevant for chromogenic prints as, unlike B&W photographs, chromogenic print stability is not as dependent on the processing methods. Rather, it is the environmental conditions of storage that mainly determine the lifetime of these prints [6, 7, 77, 78].

Though photographs are rapidly becoming ubiquitous, paper is still by far the predominant material used for documents [1]. In fact, colour photographs make up only a tiny fraction of objects in most archives; TNA's collection is currently composed of 76% paper and 0.7% photographs, of which most are B&W (2010 statistics) [79]. Their scarcity combined with their high vulnerability makes the storage of chromogenic prints in this mixed archival collection problematic, as the environmental conditions of storage are geared towards paper. Furthermore, chromogenic media have specific requirements, not least due to the inherent instability of the dyes. This instability is at odds with the requirements of archival permanence [80].

The British Standard ISO 18920:2000(E) [81] on the storage of processed photographic reflection prints, such as chromogenic prints, lists five main elements that affect the useful lifetime of photographic reflection prints in storage. These are:

- Physical damage,

- Hazards of fire, water, and light exposure,
- Fungi and other micro-organisms,
- Contact with certain chemicals in solid, liquid or gaseous form,
- T and RH of the storage environment, and other atmospheric conditions.

Physical damage is often the result of improper storage and handling. Proper storage can also severely limit the damage caused by fire, water, light exposure, and contact with chemicals [25]. It is often failure to implement programmes for preservation, security and disaster preparedness that endangers archival collections [25]. These hazards can be limited by putting in place appropriate checks, using risk assessment tools that are part of the good practice implemented in well-managed archival institutions such as TNA [10].

Looking at fungal growth, studies have shown that fungi are more likely to affect colour than B&W prints. Fungal growth may be negatively affected by reduced silver particles but not the dye particles [82]. Nevertheless, by maintaining the recommended atmospheric conditions, the environment should not be hospitable to most micro-organisms.

It is now well-recognised that photographic materials based on silver halides, such as chromogenic prints, are more sensitive to their environment than most other materials in archival storage [1]. Appropriate conditions quoted for chromogenic prints include cool (10-16 ℃), cold (2-8 ℃), or freezing (< 0 ℃) conditions for extended storage, and 30-40% RH [6, 83]. This is colder and dryer than the recommended 20 ℃ and 50% RH for other archival materials [84]. In addition to the effect on photographic materials, a risk assessment exercise carried out on TNA's collection identified atmospheric conditions, particularly relative humidity and temperature, to be of greatest concern for most of their collection as they represented over 75% of the top 10 risk factors (when not including microfilms) [10].

Light is also known to be extremely damaging to photographic materials in general and to colour photographs in particular [29]. However, in archives, photographs are stored in the dark and, therefore, light is not expected to be a major risk factor. Hence, the following sections of this chapter will deal with T, RH and atmospheric pollutants, and will examine the environmental conditions at TNA as a typical mixed archival collection.

3.2 Temperature and Relative Humidity

3.2.1 Temperature

Dye degradation is a chemical process. It is affected by factors governing the rate of chemical reactions, including temperature. The rule of thumb for objects of organic origin is that a 5 ℃ rise in temperature will half their lifetime [85]. Due to their instability cold, or at least cool, storage is generally recommended for colour photographs in order to prolong their lifetime. For medium-term storage[1], a maximum temperature of 25 ℃ (cycling of less than ± 5 ℃ over a 24 hour period) is recommended while, for extended storage[2], a maximum temperature of 2 ℃ (with cycling of less than ± 2 ℃ over a 24 hour period) is suggested [81]. Nevertheless, the relationship between temperature and stability, when combined with other environmental factors such as humidity and pollutant concentration, is not clearly known.

3.2.2 Humidity

The British Standard ISO 18920:2000(E) [81], when suggesting storage practices for photographic reflection prints, specifies that, in the case of RH in storage environments, great care must be taken not to exceed the limits (20-50% RH for medium-term storage; 30-40% RH for extended storage). Although the exact role of moisture is not well understood, the reason for these limits is that, in general, moisture promotes the rate of degradation [76, 86].

The moisture content of materials depends primarily on their composition and on the RH of the environment in which they are situated. A chromogenic print is a multi-layer structure composed of materials that may react differently to the same RH due to different material hygroscopicity[3] [29, 87]. Thus, the different layers may expand or contract at different rates, introducing stresses and strains in the print. This leads to physical damage.

[1]Medium-term storage conditions are suggested for preserving information for a minimum of 10 years [81].

[2]Extended-term storage conditions are suggested when it is desired to preserve information for as long as possible. This was formerly known as archival storage [81].

[3]Hygroscopy: Ability of a material to attract and hold water.

In colour photographs, RH is also known to affect the emulsion used, generally gelatine, as well as the dyes. At high RH, gelatine becomes softer. The dyes are then able to migrate, causing the image to distort. Eventually, the emulsion becomes sticky, causing the photographs to adhere to other materials, and promoting the growth of fungi and other microorganisms [81]. However, these problems do not occur if the environmental conditions inside the repositories are maintained below 70% RH [88].

Low RH also damages the emulsion. As its moisture content decreases, gelatine contracts, causing the print to curl. Furthermore, it makes the print brittle and, thus, more susceptible to physical damage such as cracking [81]. This is particularly relevant at RH below 15%. Thus, problems with physical degradation are mostly relevant at the upper and lower limits of RH. However, chemical degradation also occurs when materials are stored within acceptable environmental conditions.

3.2.3 Relationship between Temperature and Relative Humidity

It is quite common to study the effects of temperature and relative humidity separately. However, T and RH are interdependent, which is why limits for the two are often quoted together [81] (Table 3.1). If the effect of these components is studied independently from each other, the synergistic impact of their effects on materials will not be observed. If their synergistic effect is identified, the balance between the two for extended lifetime may be used to advantage.

Table 3.1: Maximum temperature and average relative humidity ranges for chromogenic prints (adapted from BS ISO 18920:2000 [81]). The recommended storage conditions for other archival objects are 20 °C and 50% RH [84] for extended storage.

Condition	Medium-Term Storage	Extended-Term Storage
Maximum Temperature (°C)	25	2
Relative Humidity Range (%)	20-50	30-40

Since RH depends on T and water content in the atmosphere, it is also important that temperature is maintained as constant as possible in order to limit moisture condensation and evaporation. Therefore, although cold storage will slow down most

chemical processes causing fading, the benefits of cool storage can be reduced if the prints are repeatedly removed from storage.

3.2.4 Monitoring at The National Archives

All repositories at TNA have controlled environments with a tolerance of ± 5% RH and ± 1 °C around the set points [89] (Table 3.2). These conditions are chosen to help protect documents and artefacts for the future. The set points are kept constant throughout the year with slight variations to accommodate system limitations or the different requirements of a range of materials in the collection.

Table 3.2: Set points for the operation of the air conditioning system at The National Archives (July 2010) [89].

Repository Area	RH (%)	Temperature (℃)
All repositories Q1+Q2	50	18
Filmstore (Basement Q1)	40	17
Photostore	35	16

At TNA, monitoring of RH and T is carried out to confirm that the conditions are as required. A wireless radio-telemetry system is used, which contains 180 sensors that record conditions every 15 min [89]. Typical graphs of T and RH for the photostore and the external environment are shown in Figure 3.1.

As can be seen from this graph, T and RH are well-regulated within TNA repositories. Furthermore, although external T (9.3 ± 1.6 ℃) and RH (74.5 ± 10.2 %) fluctuate significantly, they do not affect internal T (16.1 ± 0.3 ℃) and RH (35.2 ± 1.6 %), due to mechanical regulations

While these conditions are well within the limits specified by the relevant British Standard for the storage of processed photographic reflection prints for medium-term storage [81], the temperatures are higher than those suggested for extended storage [8, 81].

However, preservation is not the only priority of archives [9]. Cold storage would, therefore, cause a number of ideological and practical issues which need to be dealt with.

First of all, storing colour photographs in cold storage would result in the prints being stored separately from the other objects to which they are related. There is, however, the concept of keeping an object and its context together; the value

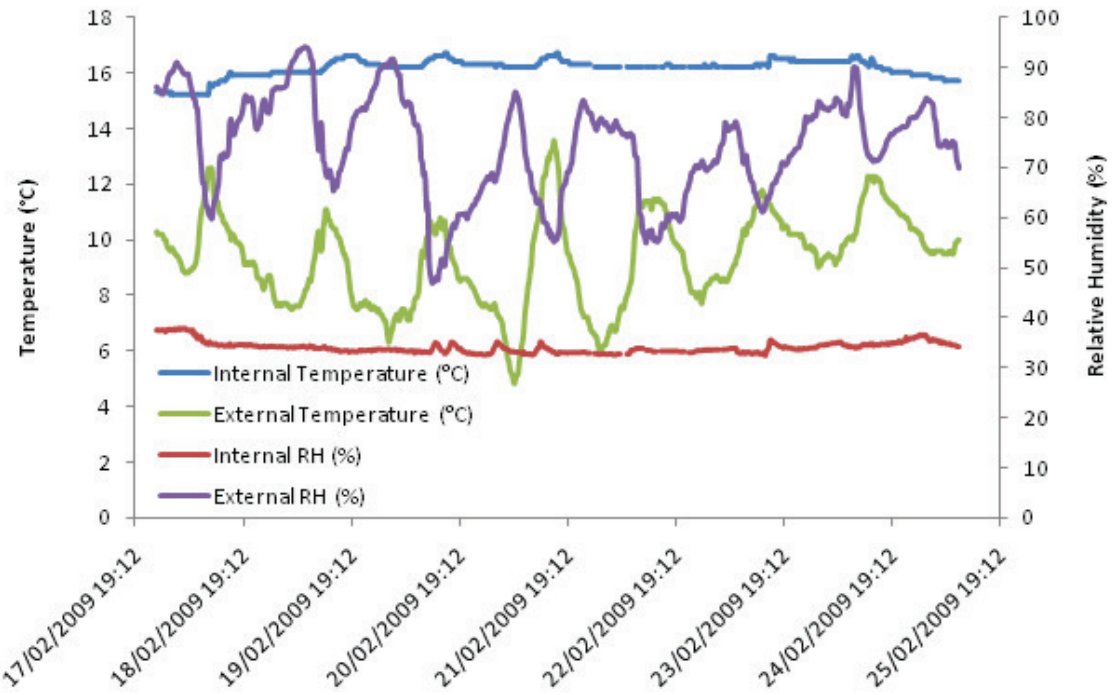


Figure 3.1: Typical external and internal temperature and RH fluctuations within the photostore. Measurements taken 17/02/2009-25/02/2009

of a colour photograph stored in conjunction with the other related material is much more than if the photograph was stored independently [25]. This is because preserving the significance of the 'whole', tends to be more than the sum of its parts [90]. Thus, it is essential to limit the removal of photographs from their context in archival collections.

On a practical level, separating material belonging in the same archival folder would extend access time to reading room users as materials from different locations need to be brought together. Nevertheless, another important priority of TNA is that of access to the collections [9]. The TNA public service standard (2010-2011) states that 99% of records should be made available to readers within 60 min [91]. However, when objects are stored at low temperatures, they need to be acclimatised for between one hour and one day [29] to the warmer conditions in the reading room. This is particularly important to avoid condensation, but achieving this often requires the use of intermediate-temperature acclimatisation chambers [2, 29].

Since the use of cold storage would increase the time between material request

and material supply to an archival user, it is only practical for objects that are not viewed regularly as otherwise the benefits of cold storage are severely reduced [29]. Moreover, this type of storage is expensive, time-consuming and labour intensive [6]. Therefore, although ideal conditions of storage of chromogenic prints for extended lifetime have been determined, a number of antagonistic requirements exist within archives than mean that these ideal conditions are not appropriate.

Furthermore, 16 ℃ is the minimum legal temperature of the work environment in the UK[4] [92]. Since the repositories are constantly accessed by staff, the temperature cannot be set lower.

3.3 Pollution Monitoring at The National Archives

It has long been known that the composition of the atmosphere, particularly the presence of pollutants[5], has a significant effect on material stability. However, pollutants in the indoor environment are often not given as much importance as T and RH, except where health concerns matter.

Pollutants can be divided into two groups:

- Particulates,
- Gaseous pollutants (eg. acidic fumes, hydrogen sulfide, ammonia, oxides of nitrogen, ozone, peroxides, sulfur dioxide, volatile organic compounds).

Particles can cause a significant amount of damage, as they can abrade surfaces, hold moisture, as well as contain acidic components that speed up degradation. However, in archives, some particulate matter is generally removed from air by filters. Additionally, objects are stored in boxes [6]. Gaseous pollutants are, therefore, of greater potential concern than particles.

Heating, ventilation and air conditioning (HVAC) systems may also have an effect on the presence of pollutants in the storage environment [6]. Gaseous impurities may

[4]The Workplace (Health, Safety and Welfare) Regulations 1992 approved code of practice [92] states: "The temperature in workrooms should normally be at least 16 ℃ unless much of the work involves severe physical effort in which case the temperature should be at least 13 ℃."

[5]A pollutant is a substance present in greater than natural concentrations that has a net detrimental effect.

be removed by filtration prior to entering archival storage. Filters for particulate matter are widely used and, in air purification systems, activated charcoal filters and other types of chemical filters are used.

Nevertheless, gaseous pollutant filters are not as common as particulate matter filters. However, even in the 1850s, before the advent of chromogenic prints, the Royal Photographic Society established the British Fading Committee to investigate the reasons for this phenomenon of photographic prints [93, 94]. This committee identified 'humid hydrogen sulfide' as one of the sources of fading [93].

Sulfur dioxide, nitrogen dioxide (and other nitrogen oxides) and ozone are among the pollutants that have been widely studied [95, 96]. Since the industrial revolution, and for a long period of time, the most significant pollutant affecting cultural heritage objects was sulfur dioxide. However, as regulations are put in place to reduce the emissions of these outdoor-generated pollutants, such as the Clean Air Act in the UK [97], it is likely that indoor sources pose a greater risk to collections due to their closer and continuous proximity to the objects [98]. These include pollutants arising both from degradation of the materials themselves, as well as from other sources such as cleaning products, paints, glues and building finishes and furnishings. Of these, acetic acid, formic acid, acetaldehyde, formaldehyde, hydrogen sulfide and carbonyl sulfide are of greatest concern to cultural heritage objects (Table 3.3).

Table 3.3: A selection of the most common pollutants in museum and archive environments, their sources, and possible effect on photographic materials [93].

Pollutant	Source	Possible Effects on Photographs
Sulfur compounds	Low quality paper enclosures	Fading of silver images
	Outdoor (combustion & natural sources)	Brown/yellow discolouration of silver images
	Adhesives	Fading of colour images
	Bioeffluents	Brittleness of paper and emulsion
	Carpets (with rubber or wool)	
NO_x	Cellulose nitrate film	Fading of silver images
	Collodion photographs	Fading of colour images
	Outdoor sources (traffic)	Brittleness of paper and emulsion
		Brittleness of nitrate film base
Other oxidising gases (eg. O_3, H_2O_2)	Outdoor (traffic and natural sources)	Fading of silver images
	Fresh paint	Fading of colour images
	Office machines	Brittleness of paper and emulsion
	Low quality paper enclosures	
Carbonyls (acids, aldehydes)	Cellulose acetate film	Brittleness and shrinkage of acetate film base
	Wood and wood-boards	
	Various building materials	Brittleness of paper and emulsion

Very limited research has been carried out to determine pollutant concentrations that are safe for the storage of photographic materials. Most guidance notes are based on what would be safe for human health, or request the use of the "best control technology" [93, 99]. In particular, knowledge of the relationship between the effects of pollutants and other environmental factors on material deterioration is limited. Therefore, it was relevant to determine the pollutant concentrations present at TNA.

3.3.1 Methodology

Pollution monitoring in the heritage environment is defined by Grzywacz [98] as "the determination of the presence of gaseous compounds in air that may damage collections, either directly or through conversion to secondary pollutants". Based on the accumulated knowledge of potentially adverse pollutant concentrations, equipment with detection limits typically at parts per billion (ppb) or lower levels are suggested for use in museums and archives, though such equipment is present in only a minority of institutions.

Conventional methods for measuring pollutants involve active sampling, where a sampling pump is used to pull air through a suitable sorbent or to a direct reading device [100–105]. Common collection intervals for active sampling are either 15 minute periods to determine the short-term exposure limit (STEL), or 8 hours for time-weighted average (TWA) concentrations [105]. Prolonged active sampling can also be performed.

However, it is not always practical to leave pumps running overnight, particularly when longer-term averages are needed. If a power supply needs to be left running overnight, safety and security concerns may make such a monitoring method untenable. In such situations, passive sampling methods are often the method of choice. These typically involve sampling periods of between 7 and 28 days [106–108]. Such sampling periods are particularly suited to museum studies where instantaneous measurements might not necessarily reflect pollutant concentrations around objects held in enclosed spaces for many years. Due to their various advantages and disadvantages, both active and passive sampling systems were used in this study.

3.3.1.1 Locations Monitored

Three different locations at TNA in Kew were monitored in 2009:

- External location: a location on the roof of the building housing the archival repositories next to a plant room was monitored for outdoor-generated pollutants. Site selection was limited to locations with available power supplies.
- Internal location - repository: The repository monitored was the photostore[6] located within repository 7A. The repository is ventilated with 30% fresh air. The remaining 70% is recirculated air. Air flow streams are pre-filtered for particulates (but not for gaseous pollutants). Approximately 3.2 air exchanges per hour (outdoor and re-circulated air) occur. Sampling was carried out at a point half-way the height of the shelving units.
- Archival boxes: cardboard archival boxes of different geometries were monitored. Three boxes were sampled for each of nitrogen oxides (NO_x), sulfur dioxide (SO_2), ozone (O_3) and volatile organic compounds (VOC). Nine boxes were monitored for acetic acid, and ten boxes were monitored for volatile aldehydes.

3.3.1.2 Monitoring Outdoor-Generated Pollutants

Sulfur dioxide (M100; limit of detection 0.4 ppb), ozone (M400; limit of detection 0.6 ppb) and nitrogen oxide (M200; limit of detection 0.4 ppb; all Teledyne API, San Diego, USA) analysers were used for active sampling and determination of the respective pollutants. The atmosphere inside and outside the repository was monitored continuously for a week and readings recorded at 15-minute intervals. Daily averages were calculated.

Inside a box the microenvironment was sampled without opening the box for one parameter per box only (either NO_x, O_3 or SO_2, Table 3.4). Sampling was carried out through a star cut made in the box. After the readings stabilised (approximately 30 seconds), the values obtained were averaged and the standard deviation was calculated. Due to the pump flow of 500 mL/min and the limited air volume within the boxes, the readings slowly changed after 2 min, which is when the measurements were discontinued.

[6]The 'Robot Room' since October 2009.

Table 3.4: Boxes used for sampling, and the pollutants sampled. The numbers in the pollutant column refer to the box number for that pollutant as referred to in Table 3.7

Shelf	Collection	Box No.	Dimensions (cm)	Pollutant
764	INF10	130-135	37.5 x 27 x 11	SO_2 - 1
763	INF10	54-59	36.5 x 26.5 x 11	O_3 - 1
715	CN5	7-12	39.5 x 32 x 10.5	NO_x - 1
739	CO1069	899-901	39.5 x 48 x 10.5	SO_2 - 2
747	Copy 1	373 part 3	70 x 47 x 8.5	O_3 -2
715	CN4	1-6	39.5 x 32 x 10.5	NO_x -2
730	WO316	3-8	39.5 x 29.5 x 10.5	SO_2 - 3
739	CO1069	909	41 x 28 x 8.5	O_3 - 3
738	CO1069	831-834	44.5 x 29 x 8	NO_x - 3

3.3.1.3 Monitoring of tVOCs

A ppbRAE 3000 (10.6 eV lamp; resolution 1 ppb; range 1 ppb - 10000 ppm; RAE Systems, San Jose, USA) portable continuous VOC monitoring instrument was used to measure total VOC (tVOC) concentrations. tVOCs do not include formaldehyde and acetic acid as VOCs with ionisation energy higher than 10.6 eV cannot be detected using this instrument. The instrument was calibrated against the calibration gas isobutylene, therefore, all measurements express values of tVOCs in ppb of the calibration gas.

Continuous monitoring was carried out inside the photostore for a week and readings were taken at 15-minute intervals. Microenvironments inside boxes were monitored as described above for other pollutants.

3.3.1.4 Monitoring Volatile Aldehydes

UME^{x}100 formaldehyde samplers (limit of detection 0.2 ppb; SKC, Blandford, UK) were used as received for the determination of formaldehyde, acetaldehyde, hexanal and furfural. The samplers, which contain a solid support impregnated with 2,4-dinitrophenylhydrazine (DNPH) that reacts with aldehydes to form their corresponding hydrazones, were exposed to the environment for 7 days.

3 samplers were placed on empty shelves, together with 2 unopened samplers (control), in the middle of the repository. Another 10 samplers were placed in boxes situated in different parts of the photo store and repository 7B (Table 3.5). Care

was taken to open the boxes as little as possible to insert the samplers. Blanks (unopened samplers) were positioned in the vicinity of the samplers to measure the repository environments.

Table 3.5: Boxes selected for sampling using UME^x samplers for 7 days.

Box	Shelf	Collection	Box No.	Dimensions (cm)
1	761	Copy 1	516	37 x 24.5 x 8.5
2	723	ADM244	1-2	40 x 27 x 11
3	763	INF9	1301-1320	39 x 32.5 x 8
4	750	copy 1	99	34 x 27 x 8.5
5	744	copy 1	384 parts 3-4 end	64.5 x 34.5 x 8
6	737	CO 1069	640	44 x 32 x 3
7	733	CO 1069	168	40 x 31.5 x 5
8	531	CO 324	167	40 x 29.5 x 5.5
9	594	ADM20	301	62 x 47 x 6
10	669	F.E.C. 2	85-87	40 x 29 x 14

After sampling, the samplers were sent for analysis to the University of Ljubljana. There, the hydrazones were eluted from the samplers using 10 mL of acetonitrile, and the solutions were analysed by high performance reverse-phase liquid chromatography (Waters Alliance 2690 equipped with 2487 Dual wavelength absorbance detector; software: Millenium) using a Phenomenex Gemini C18 column 250 mm × 4.6 mm with 5-µm stationary phase size. Two solutions were used for gradient elution: Solution A contained 45% acetonitrile and 55% acetic acid in water (0.2% v/v); Solution B contained 100% acetonitrile. The starting eluent was 100% of Solution A for 10 min following which a linear gradient was applied over 30 min until the eluent contained 10% Solution A and 90% Solution B. This eluent mix was held for a further 15 minutes. The eluent flow rate was 1 ml/min. Spectrophotometric detection of the DNPH derivatives was performed at 365 nm and quantification was carried out using calibration curves for standard hydrazone solutions (T011/IP-6A Aldehyde/Ketone-DNPH; Supelco, Bellefonte PA, USA) of each corresponding aldehyde. Linear calibration curves ($R^2 > 0.9995$) were used to calculate sample concentrations.

Concentrations of formaldehyde (in volume/volume ppb) in the air were calculated according to the SKC manual [109]. However, the 7-day sampling rate is given only for formaldehyde (20.4 mL/min). For other aldehydes, adjusted sampling rates were estimated according to sampling rate data as made available by Radiello [110].

Despite the different geometries of SKC and Radiello samplers, the sampling ratios for different compounds vs formaldehyde, for the two geometries, were considered to be comparable. The ratios calculated as adjustment factors were as follows: 0.8 for acetaldehyde, and 0.2 for furfural and hexanal, relative to the sampling rate for formaldehyde, for the SKC sampling geometry. While there are no sampling rates available for furfural by Radiello, the correction factor 0.2 was used, by analogy with other aldehydes of similar molecular weight and size.

Standard deviation was always calculated based on the results obtained from three samplers exposed in the same location (repository), except when these were placed in boxes, where one sampler per box was used and the values from different boxes were averaged.

3.3.1.5 Monitoring of Acetic Acid

Eleven passive acetic acid sampling tubes (limit of detection: 17 ppb; University of Stratchlyde) were deployed (9 in archival boxes (Table 3.6), and 2 in the repository environment) together with 3 unopened tubes (controls) in the repository. Then, they were analysed according to the established method [106] at the University of Stratchlyde. Dimethoxyethane replaced glycerol as the wetting agent during impregnation of filter paper discs, together with 1 M KOH. This disc was placed in a 7.1 cm long/1.1 cm diameter poly(methyl methacrylate) tube and exposed to the environment for 40 days. The obtained extracts were later analysed using ion chromatography.

Table 3.6: Boxes selected for sampling using acetic acid passive diffusion tubes for 40 days.

Shelf	Collection	Box No.	Dimensions (cm)
750	Copy 1	100	36.5 x 34 x 11.5
744	Copy 1	384 parts 1-2	64.5 x 34.5 x 7
738	CO1069	730	40 x 31 x 5
733	CO1069	205	44 x 39 x 8.5
716	CN11	1-10	39.5 x 29 x 11
531	CO324	168	42 x 6.5 x 29
594	ADM20	302	30 x 10 x 45
669	FEC2 74	1-18 end	25 x 18.5 x 37
139	ADM22	260	40 x 8 x 52

3.3.2 Results

3.3.2.1 Outdoor-Generated Pollutants

As expected, outdoor-generated pollutants were more prevalent in the external environment (Figure 3.2) than in the internal environment (Figure 3.3). Also, the transfer of pollutants indoors is such that concentration changes internally are smoother than in the external environment, indicating that the building may be acting as a buffer. At this point it is also worth highlighting that the internal[7] and external[8] environments were monitored on two subsequent weeks. However, this is not expected to have affected the results significantly.

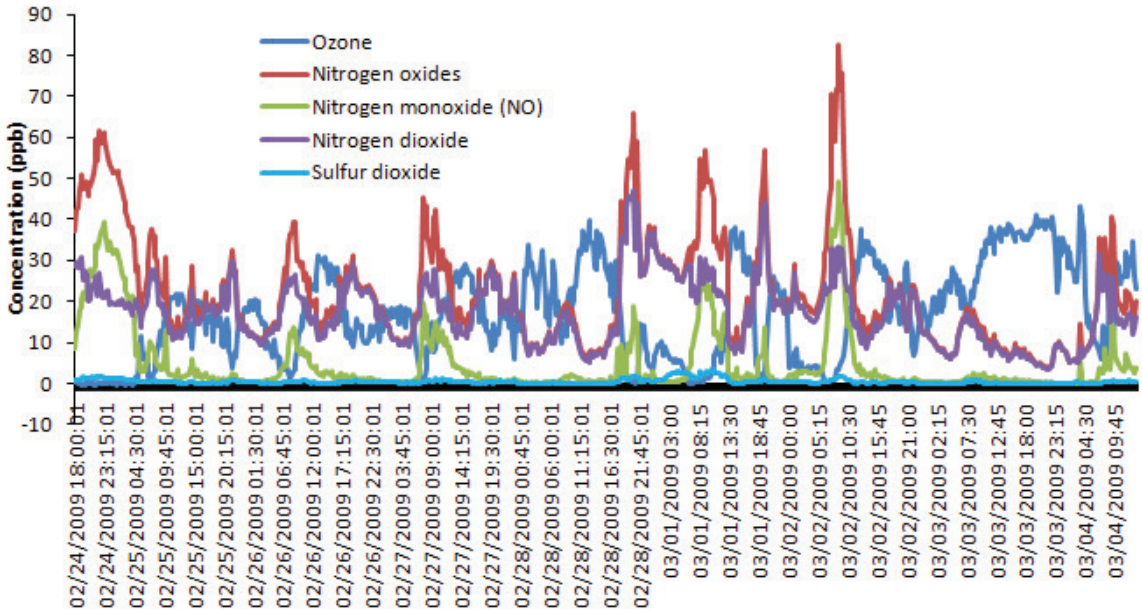


Figure 3.2: Results of a week of monitoring the outdoor-generated pollutants ozone (O_3,), nitrogen oxides (NO_x), nitrogen monoxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) externally to the TNA building between 24^{th} February 2009 and 3^{rd} March 2009.

Monitoring inside the archival boxes showed than nitrogen monoxide (NO) is the prevalent pollutant (Table 3.7).

[7]During the monitoring period, the daily mean temperature fluctuated between 8.8 and 10.3 ℃ (min: 6.5 ℃; max 13 ℃) and the mean humidity fluctuated between 65 and 83%.

[8]During the monitoring period, the daily mean temperature fluctuated between 8.6 and 10.3 ℃ (min: 4.7 ℃; max: 11.6 ℃) and the mean humidity fluctuated between 64 and 83%.

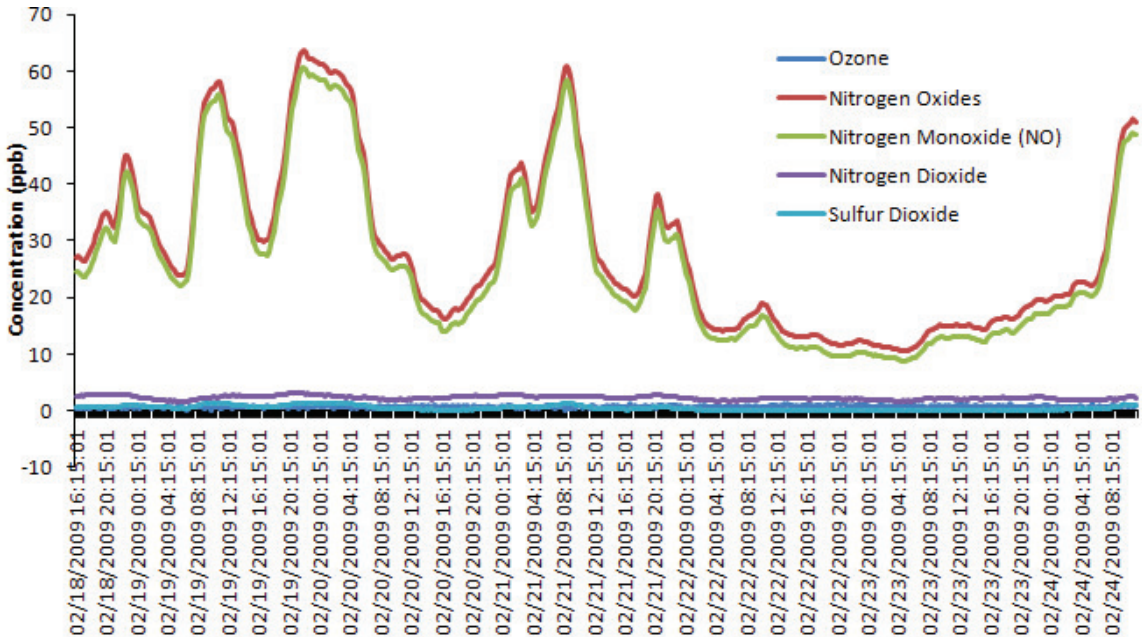


Figure 3.3: Results of monitoring outdoor-generated pollutants ozone (O_3,), nitrogen oxides (NO_x), nitrogen monoxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) inside the photostore in repository 7A between 18^{th} and $24t^{th}$ February 2009.

Table 3.7: Results for the concentrations of outdoor-generated pollutants ozone (O_3,), nitrogen oxides (NO_x), nitrogen monoxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) inside archival boxes. Ambient refers to the concentration within the repository just prior to measurement of concentrations in the archival boxes.

Location	concentration (ppb)				
	O_3	NO_x	NO	NO_2	SO_2
Box 1	0.3	13.0	10.2	2.8	0.0
Box 2	0.4	12.9	10.4	2.5	0.0
Box 3	0.5	12.7	10.4	2.2	0.0
Average	0.4 ± 0.1	12.9 ± 0.2	10.3 ± 0.1	2.5 ± 0.3	0 ± 0
Ambient	0.6	12.8	10.2	2.6	0.0

3.3.2.2 tVOCs

tVOCs were monitored inside the repository (Figure 3.4) and inside archival boxes (Table 3.8). Sharp peaks during the week-long monitoring campaign were found to correspond with cleaning activities.

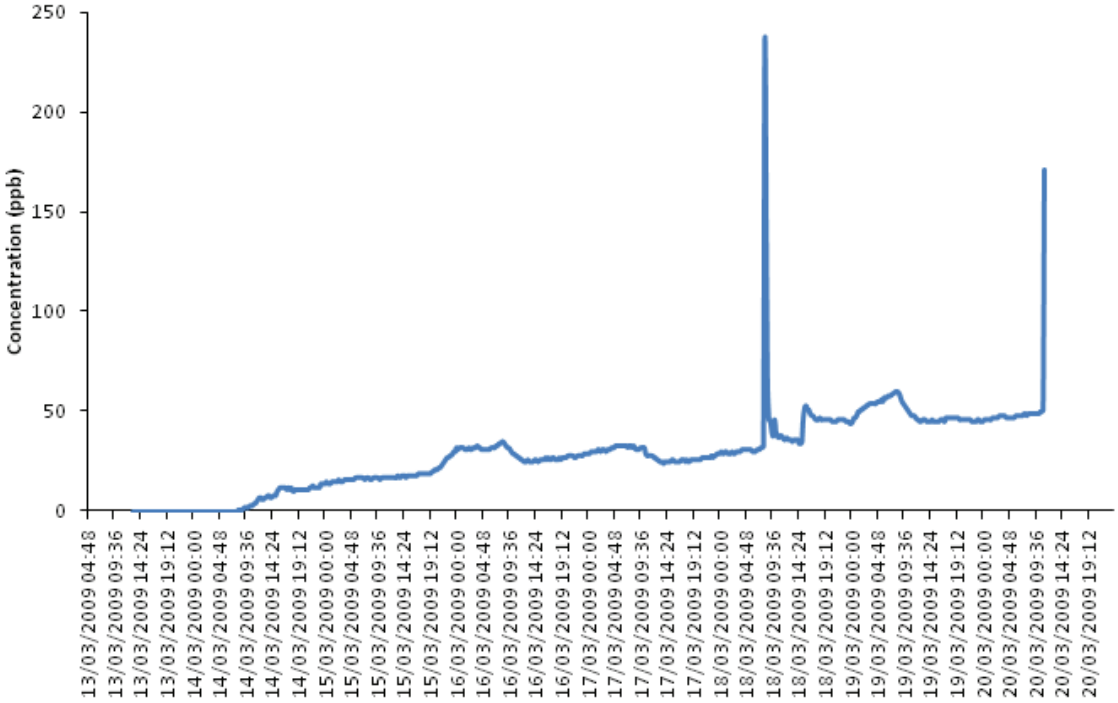


Figure 3.4: tVOC concentrations in the TNA repository between the 13^{th} and 20^{th} of March 2009.

Table 3.8: Results for tVOC concentrations inside boxes.

Shelf	Collection	Box No.	tVOC (ppb)
764	INF10	130-135	74
763	INF10	54-59	72
715	CN5	7-12	65
739	CO1069	899-901	71
715	CN4	1-6	73
730	WO316	3-8	69
739	CO1069	909	68
738	CO1069	831-834	70
	Average		69 ± 5

3.3.2.3 Volatile Aldehydes

Volatile aldehydes, specifically formaldehyde, acetaldehyde, furfural and hexanal, were sampled inside 10 archival boxes and the repository environment (Table 3.9). In all cases, hexanal was found at concentrations lower than 0.1 ppb. The concentrations in the archival boxes and in the repository environment are statistically different for formaldehyde, $F(1, 12) = 19.7$, $p < 0.05$. Differences in concentration of the other compounds are not statistically significant, $F(1, 12) = 0.85\text{-}1.85$, $p > 0.05$.

Table 3.9: Volatile aldehyde concentrations measured in 10 boxes and in the repository environment.

	Concentration (ppb)		
Box	Formaldehyde	Acetaldehyde	Furfural
1	1.2	0.6	< 0.1
2	3.3	1.5	0.1
3	2.9	0.7	< 0.1
4	2.7	0.9	< 0.1
5	3.7	1.3	< 0.1
6	2.4	0.6	< 0.1
7	2.7	1.0	0.2
8	1.5	0.7	< 0.1
9	1.6	0.6	< 0.1
10	3.2	0.6	< 0.1
repository env	4.8 ± 0.2	1.0 ± 0.1	< 0.1

3.3.2.4 Acetic Acid

As for volatile aldehydes, acetic acid was also monitored in archival boxes and in the repository environment (Table 3.10). The average concentration was of 70 ± 61 pbb in the archival boxes and 19 ± 6 pbb in the repository environment.

3.3.3 Discussion

While temperature and RH are routinely monitored in most heritage institutions, including TNA, pollutant monitoring is much less common [98, 111]. In order to identify the pollutants causing degradation of chromogenic prints, extensive pollutant monitoring was performed, both externally to the TNA building and within a

Table 3.10: Acetic acid concentrations in the repository environment and 9 archival boxes.

Shelf	Collection	Box No.	Concentration (ppb)
750	Copy 1	100	13.6 ± 2.4
744	Copy 1	384 parts 1-2	20.6 ± 0.4
738	CO1069	730	40.5 ± 7.7
733	CO1069	205	150.9 ± 0.4
716	CN11	1-10	36.5 ± 0.8
531	CO324	168	151.3 ± 0.4
594	ADM20	302	31.6 ± 0.4
669	FEC2 74	1-18 end	32.4 ± 0.4
139	ADM22	260	150.5 ± 2.0
repository env			19.4 ± 0.3

repository. It was also essential to identify the pollutants within archival boxes to understand the microclimates of chromogenic photographs.

3.3.3.1 Monitoring the External Environment

In an urban environment, such as London, the outdoor-generated pollutants found indoors are typically the major pollutants found in the external environment. They are produced primarily by anthropogenic activity, which can be observed from their diurnal cycles where daily maxima and nightly minima coincide with the extent of human activity (Figure 3.5) [112]. In particular, these cycles are often driven by the level of motor vehicle traffic; the major source of nitrogen oxides and sulfur dioxide is the burning of fossil fuels, while ozone is often produced as a result of ongoing reactions with other pollutants and light. Hence, SO_2 and NO_x are primary pollutants, while O_3 is a secondary pollutant depending on insolation.

The diurnal cycles, as shown in Figure 3.5, were clearly evident from the results of monitoring externally to the repositories (Figure 3.2). Most NO peaks occur in the morning hours (7:30am to 9:30am), with some peaks occurring during the evening (mainly 7:45pm to 8:45pm). High levels are, thus, observed during the morning rush hour while lower levels occur during the evening rush hour (as this is generally spread out over a longer time-scale). Namely, during the evening and the early morning period of heavy commuter traffic, nitrogen monoxide (NO) concentrations build up [113, 114]. However, in daylight, conversion between its two main forms, NO and NO_2, occurs rapidly:

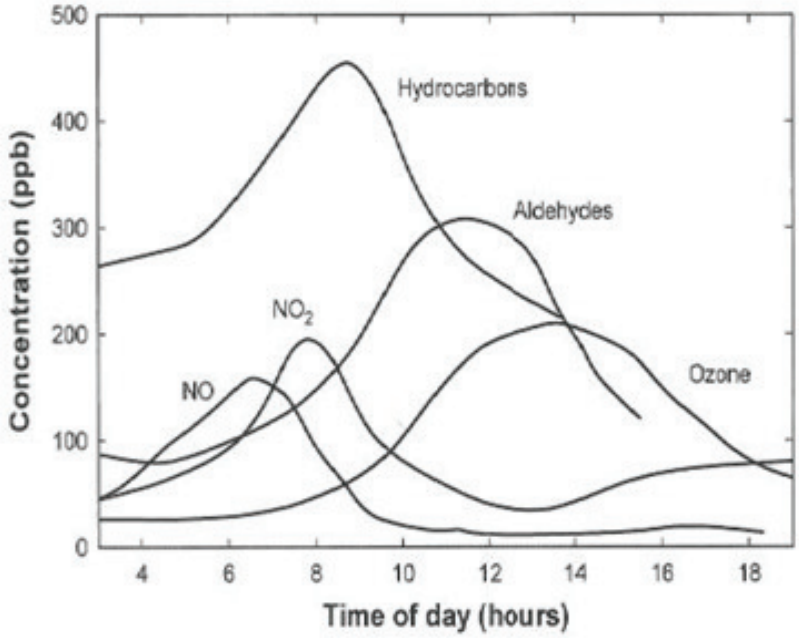


Figure 3.5: Daily cycling of pollutants typical in an urban environment [111].

$$\mathrm{NO} + [\mathrm{O}] \xrightarrow{h\nu} \mathrm{NO_2}$$
$$\text{e.g. } \mathrm{HO_2\cdot} + \mathrm{NO} \xrightarrow{h\nu} \mathrm{HO\cdot} + \mathrm{NO_2}$$

Thus, NO_2 is formed in the atmosphere by oxidation e.g. with ozone, of NO, with very little direct emission [111]. In fact, the concentration of NO_2 typically peaks after NO, at which point the NO concentration already starts to decrease, as this is converted into NO_2 [112, 114].

A second increase in NO_x is also often associated with the evening rush hour. Depending on the day length, NO from evening emission may be converted into NO_2, or remain in its original form. Nevertheless, this peak is never as big as the morning peak. Due to the short time-scale of these photochemical reactions, regions downwind of major NO_x sources, even if rural, tend to be the more severely affected by secondary pollutants, including ozone or particulate matter [112].

However, as seen in Figure 3.2, nitrogen oxides are not the only atmospheric pollutants that undergo daily cycling. In the presence of hydroxy radicals and hydrocarbons, ozone production is catalysed [112]. Ozone (as nitrogen dioxide) is a photochemically produced secondary pollutant, having a clear maximum in the middle of the day, particularly in conditions of high surface temperatures from strong

solar radiation [114]. However, this will depend on the amount of hydrocarbons and other energy-absorbing bodies (M) in the atmosphere, as photochemical processes (reactions with peroxy radicals) are responsible for the formation of the ozone and oxidation processes:

$$\mathrm{NO_2} \rightarrow \mathrm{NO} + [\mathrm{O}]$$
$$[\mathrm{O}] + \mathrm{O_2} \rightarrow \mathrm{O_3}$$
$$\text{e.g. } h\nu + \mathrm{NO_2} \rightarrow \mathrm{NO} + \mathrm{O}\cdot$$
$$\mathrm{M} + \mathrm{O}\cdot + \mathrm{O_2} \rightarrow \mathrm{O_3} + \mathrm{M}^*$$
$$\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

These processes are evident when the values of the external concentrations of NO_x and O_3 are plotted on the same graph. The concentrations of NO_x and O_3 fluctuate in exactly the opposite directions (Figure 3.6), indicating that ozone is produced as a secondary pollutant from nitrogen oxides. In view of the results presented in this thesis, this also shows that, although the plant room was close to the sampling location, the recorded O_3 was mainly not a result of its proximity, but a result of the photochemical reactions outlined above.

In urban areas, ozone concentrations diminish during the night due to the absence of solar radiation. In the dark, the following reaction takes place [115]:

$$\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

Furthermore, ozone also converts leftover NO_2 to NO_3, a free radical, which is an effective oxidant during the dark stage. However, it is photo-unstable and immediately decomposes in daylight.

It should also be noted that, although for a long time sulfur dioxide was considered the main pollutant of interest to conservation, regulations put in place to reduce its emissions [97] have been successful as shown by the very low concentrations of sulfur dioxide monitored in the external environment. It is very interesting to note that SO_2 concentrations very closely followed those of NO_x (Figure 3.7). This indicates that the main source of SO_2 is the burning of fossil fuels (particularly motor vehicles).

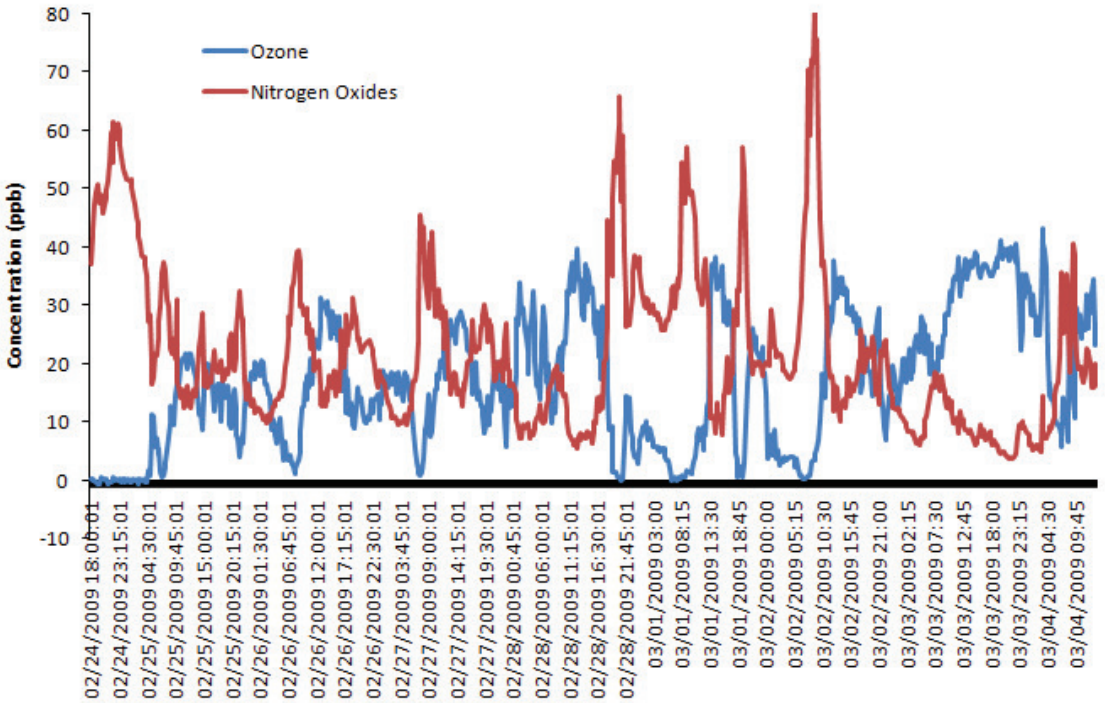


Figure 3.6: Fluctuations of concentrations of O_3 and NO_x in the environment external to the repository.

3.3.3.2 Monitoring of the Repository Environment

Outdoor-Generated Pollutants

Clear differences emerged between concentrations of outdoor-generated pollutants in the external (Figure 3.2, p. 73) and internal (Figure 3.3, p. 74) environments. In particular, sulfur dioxide, ozone and nitrogen dioxide were found in much lower concentrations internally, and were also much more stable. This can be explained by their high reactivity with the indoor surfaces. This occurs even in buildings without any filtration systems in place [116].

Inside the repository, the major pollutant was NO, with the NO_x and NO curves changing practically in synchrony. NO seemed to peak during night time, possibly because photochemical reactions causing its breakdown were absent and, hence, there was more time for it to ingress indoors. Furthermore, it would take some time for the pollutants to filter into the building. It also needs to be noted that lower concentrations of externally-generated pollutants were recorded over the weekend than during the week, either reflecting lower traffic density or a lower exchange rate

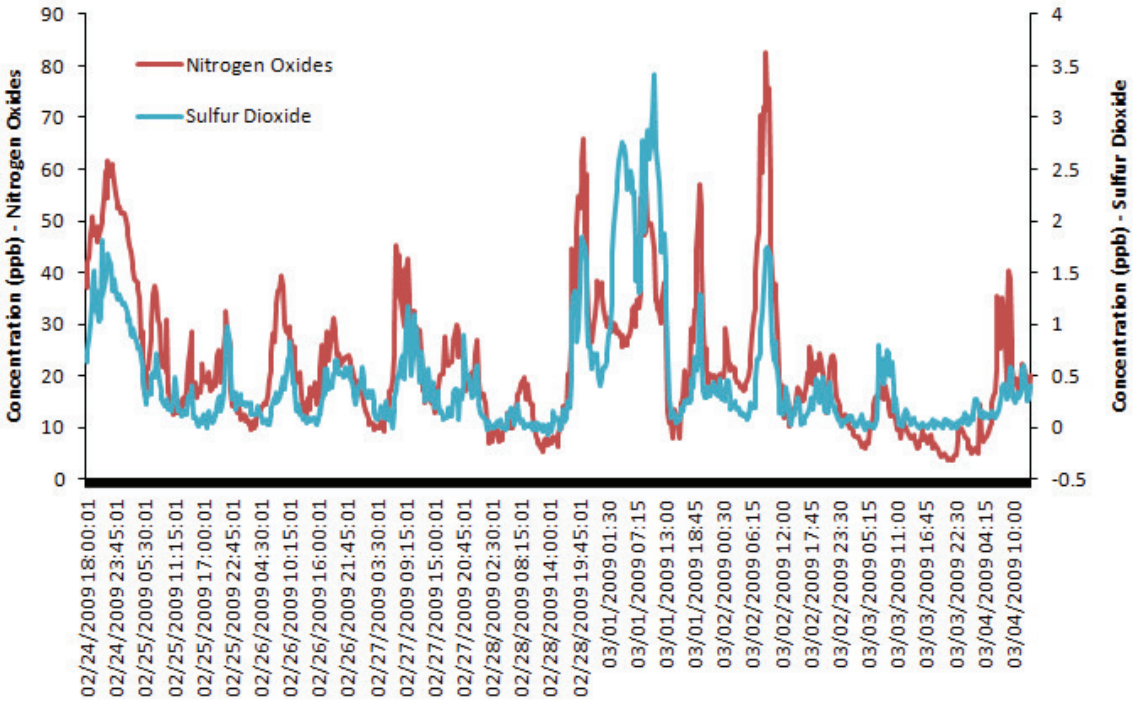


Figure 3.7: Fluctuations of concentrations of NO_x and SO_2 externally to the TNA repository.

with other areas inside the building as the repository investigated is only connected to the rest of the repositories via a door that is kept closed.

The diurnal changes observed inside the repository were much smoother than outside. This is possibly as a result of the time needed for the gases to diffuse into the repository, which is dependent on the ventilation system and protects the internal environment from sharp peaks.

Indoor-Generated Pollutants

The most common pollutants originating within buildings are volatile organic compounds, or VOCs. VOCs are organic compounds that contain at least one carbon atom in their molecular structure, which are present in gaseous form at room temperature. If the air exchange rate is high, concentrations can be maintained at levels comparable to those encountered outdoors. However, in closed storage environments such as repositories and particularly in archival boxes, VOCs can accumulate [111].

The VOCs known to have a significant effect on heritage materials are aldehy-

des, such as formaldehyde and acetaldehyde, and acids such as acetic and formic acids [111]; acetic acid, formic acid and formaldehyde tend to be the most common and damaging inside buildings housing heritage materials (Table 3.11) [111, 116]. Aldehydes can also be oxidised to carboxylic acids, particularly in high RH or in the presence of strong oxidants, which lead to an increase in acid concentrations [111].

Table 3.11: The main VOCs and their effect on materials in heritage environments (adapted from Blades et al. [116]).

Species	Effects	Indoor Pollution Source	Interior	Enclosures
Formic Acid	Attacks calcareous materials such as seashells Corrodes certain metals, especially lead, zinc and copper alloys with high lead content Attacks mineralogical specimens	Drying paint, oxidation of formaldehyde Some woods (but lower emissions than acetic acid)	< 30 ppb	100s-1000s ppb in cases with internal sources
Acetic acid	Attacks calcareous materials such as seashells Corrodes certain metals, especially lead, zinc and copper alloys with high lead content Attacks mineralogical specimens May attack paper, pigments and textiles	Decomposition of cellulose acetate film Wood and wood products, adhesives and sealants		
Formaldehyde	May be oxidised to formic acid	Wood particleboard products, resins, some thermosetting plastics	< 30 ppb	100s-1000s ppb in cases with internal sources

As can be seen from the results obtained for tVOCs (Figure 3.4, p. 75), the VOC levels increased over the whole week at a steady rate, from around 0 ppb over the first few hours to around 50 ppb after one week. This did not seem to be the consequence of a drift in the instrument's baseline as, after a week of monitoring, the instrument still gave a zero reading when attempting zeroing through a VOC-scrubbing tube and gave the same measurement following the zeroing process.

This drift could be a result of accumulation of pollutants inside the photostore repository, which is not used much and is also much smaller than other repositories. However, at the start of monitoring, the door had to be kept open to bring in the equipment that would have led to effective air exchange with the larger and better ventilated repositories.

Peaks are also observed at two points in the monitoring period. This was found to coincide with cleaning staff entering the repository and using cleaning products, including a spray for cleaning surfaces being used.

3.3.3.3 Pollutant Concentrations Inside Archival Boxes

The microenvironment inside archival boxes is of major interest as boxes are a physical barrier to the migration of compounds and can act as an absorbent. VOCs and outdoor-generated pollutants were measured in archival cardboard boxes of various sizes and loading ratios, and filled with archival folders of various compositions in order to obtain representative pollution profiles.

Outdoor-Generated Pollutants

Outdoor-generated pollutant concentrations within the archival boxes were lower than those found externally. In particular, no sulfur dioxide was recorded, which indicates that sulfur dioxide is effectively absorbed and that it cannot be measured. This could indicate that the pollutant is effectively absorbed and, hence, causes significant damage. However, because sulfur dioxide was not found in high concentrations within the repository itself indicates that this is not the case. Therefore, it is unlikely to play a part in the degradation of materials in the archives. Ozone and nitrogen dioxide were also present in lower concentrations than those found externally. However, the major outdoor-generated pollutant identified within the archival boxes was nitrogen monoxide, possibly due to its lower reactivity.

Indoor-Generated Pollutants

The indoor-generated pollutants were found in much higher concentrations within the archival boxes than outdoor-generated pollutants (Figure 3.8), particularly acetic acid, which was present in the highest concentrations within the archival boxes. The results of acetic acid measurements also showed high variability. The acid is a known product of degradation of organic materials, including paper [117–122]. Hence, this high variability is the likely result of different material types in the individual archival box, as was noticed for aldehydes in archival environment [123].

The average concentration of aldehydes inside boxes was found to be lower than that found in the immediate surrounding environment (TNA repository) and the

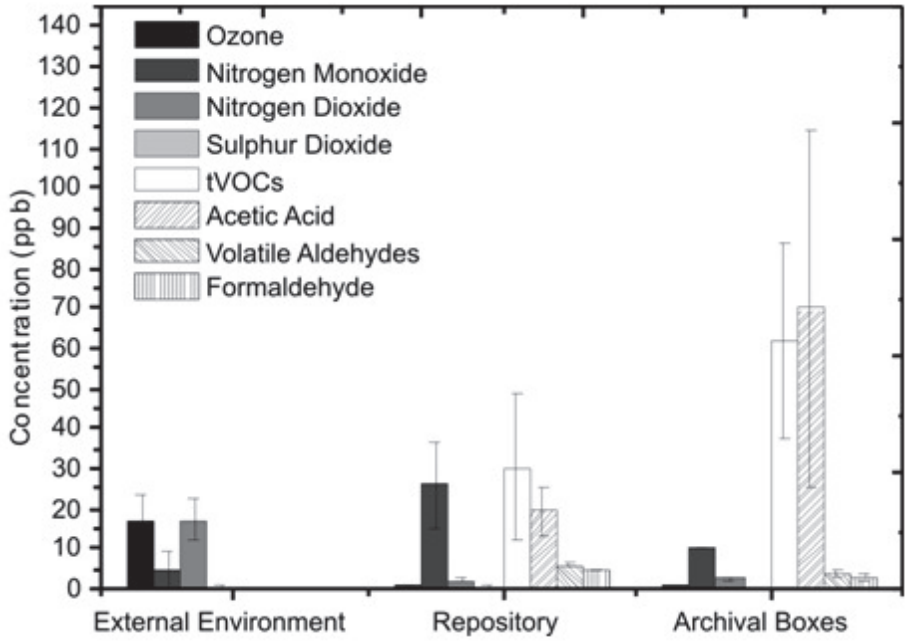


Figure 3.8: Concentrations of pollutants inside and outside the TNA repository and inside archival boxes at TNA. No measurements of volatile aldehydes and acetic acid were taken outside the repository as they were not expected to be found at measurable concentrations. The error bars represent standard deviation. For O_3, NO, NO_2 and SO_2, and tVOCs the values for the 'External Environment' and the 'Repository' represent daily averages and for 'Archival Boxes' they represent short-term averages; acetic acid passive samplers were exposed for 40 days while the ones for aldehydes were exposed for a week.

major difference was in the concentration of formaldehyde. It is, therefore, possible that the source of formaldehyde is found in the environment external to the boxes. Although the variability of results for formaldehyde is not as high as that for acetic acid, it seems to indicate that the profile and concentrations of aldehydes depend upon the composition of paper stored inside boxes and, certainly, also on the time the particular box remained closed prior to the measurement, as this affects the accumulation of VOCs. Also, the air exchange rate can vary from box to box.

3.3.3.4 Comparison of Pollutant Concentrations across the Locations

The results of measurements inside and outside the repository (externally to the building, 'External Environment'), as well as inside boxes are shown in Figure 3.8.

As expected, the major pollutants outside the repository were the outdoor-

generated pollutants O_3, NO and NO_2. Even though there is no major traffic source close to the TNA, a typical diurnal urban pollution pattern [124] was detected. Inside the repository, concentrations (except that of NO) were lower than outside, which is in line with other studies [125–127], and is the result of reaction and removal through absorption by material surfaces. The concentrations of outdoor-generated pollutants were very low inside archival boxes (10.3 ± 0.1 ppb NO, 2.5 ± 0.3 ppb NO_2, 0.4 ± 0.1 ppb O_3), indicating that the boxes provide a degree of protection from these pollutants.

Concentrations of VOCs at the different locations were also examined. No significant concentration of tVOCs was found in the external environment. This is in contrast to the situation inside the repository ($\sim$ 30 ppb), while even higher concentrations of tVOCs were found inside the boxes ($\sim$ 60 ppb). Using passive sampling, concentrations of acetic acid and aldehydes, inside and outside the boxes, were also measured. While the concentration of aldehydes inside the repository and inside the boxes was quite similar, the situation was different for acetic acid as it was found to be much more abundant inside the boxes than in the repository.

A comparison of the measurement uncertainties is also of interest. Those of traffic generated pollutants are very low compared to those of volatile aldehydes, tVOCs and acetic acid. This indicates that traffic generated pollutant concentrations inside boxes are unaffected by the different geometries, loading ratios, stored archival materials in the boxes, and the time since last opening. In contrast, the very high uncertainties in concentrations of acetic acid and tVOCs are of high importance and can only be the consequence of the variability of the archival materials stored inside boxes.

3.4 Conclusion

TNA, though not in the centre of London, still experiences pollutant concentrations and patterns typical of an urban area. The situation inside the repositories was, however, of the main interest: the concentrations of SO_2 and particularly of O_3 were much lower than the values recorded externally. However, the concentrations of NO_x did sometimes match concentrations observed externally. Nevertheless, much smoother fluctuations were found inside the repository indicating that the building had a significant effect on the buffering of changes in pollutant concentrations.

Measurement of pollutant concentrations in archival boxes were of relevance since this is the microclimate experienced by archival records. The boxes act as a further barrier and, in particular, sulfur dioxide was not recorded in any of the boxes.

The significantly higher concentrations of tVOCs and acetic acid inside the archival boxes is, however, of concern. With the decline in outdoor-generated pollutant concentrations as a result of strict environmental regulations in the last decade, the concentration of indoor-generated pollutants is becoming ever more relevant. There are reports on the effect of VOCs on heritage materials such as colourants, glass, and metals [128–130]. Yet, studies of the effects of many VOCs on the stability of heritage materials still need to be carried out, particularly as indoor environments could act as reaction vessels, resulting in reactions that might otherwise not be possible [131].

As yet, no guidelines have been specified for VOC concentrations in buildings housing heritage materials [101, 116]. Research has yet to be done on the potential damage caused by VOCs on heritage materials in libraries and archives, including potential synergistic effects with other environmental conditions. While this thesis addresses chromogenic prints, there are other heritage materials that could be studied.

On the basis of results in this Chapter, VOCs (particularly acetic acid and formaldehyde) and NO_2 were identified for further investigation in this research. NO_2 was investigated due to its higher reactivity, when compared to NO.

Chapter 4

Materials Research

To provide guidance on conservation measures, it is necessary to understand the effect of deterioration agents on the rate of degradation of heritage materials [132]. This can be accomplished if scientific methods for material characterisation are available. The current routinely used methods for characterisation of photographs are visual analysis and optical microscopy [2]. However, with these methods it is rarely possible to measure changes in a material, which is important in degradation studies.

As outlined in Chapter 1 research relating to material characterisation is the second line of research relating to the lifetime of chromogenic prints. Hence, this Chapter discusses two analytical methods developed as part of the research project.

As was discussed in Chapter 3, environmental conditions may affect both the chemical and physical nature of materials. However, the analysis of changes in chemical properties, rather than physical or mechanical properties, is often more pertinent [76, 133] since degradation is frequently a result of irreversible chemical reactions. Changes in molecular composition of the artefact lead to physical changes [134] that tend to be measurable only after considerable chemical decay had occurred first. Therefore, chemical properties often provide information about deterioration with higher precision and sensitivity, while requiring smaller samples [76, 133, 135]. Hence, monitoring of chemical properties may be used as an early warning system.

When carrying out chemical analyses, the philosophy of minimum intervention is key [136]. Even though the use of non-destructive/non-invasive methods is not always possible or practical, efforts should be made to identify, use and develop such methods. Non-destructive methods also allow for repeated measurements of

the same sample, which is ideal for long-term studies. Hence, this chapter discusses the efforts to develop non-destructive methods for the characterisation of different aspects of chromogenic prints.

The first method looks at monitoring dye concentrations in chromogenic prints during degradation (Section 4.1). The development of a chromatographic technique is first discussed and the results then compared to those obtained with colorimetry, while discussing why such a method would be appropriate for historic objects.

Section 4.2 discusses the development of a tool for dating chromogenic prints. In particular, it discusses the current methodologies used to date photographic prints and outlines the benefits of near infrared spectroscopy combined with multivariate analysis as an alternative.

4.1 Monitoring Dye Concentrations

Quoting Jean-Louis Bigourdan, a fellow at George Eastman House, International Museum of Photography and Film, "wherever there are colour materials, the vulnerable component will be the dyes" [137]. Thus, it is essential to understand what agents lead to changes in chromogenic dyes. Therefore, a method is needed that enables us to monitor dye concentrations.

Chromatographic techniques are typically employed for the characterisation of photographic dyes [4]. Chromatography allows chemical compounds to be separated depending on their rate of migration across the boundary of two phases representing specific chemical environments. This allows the dyes to be isolated and, subsequently, analysed. Liquid chromatography is wide-spread in the photographic industry including in the separation of dyes, using techniques such as thin-layer chromatography [4], High Performance Liquid Chromatography (HPLC) [4, 138], and capillary electrochromatography [138].

However, chromatography is a destructive analytical technique. This is a significant limitation when working with heritage materials and an analytical procedure had to be identified that could monitor changes in dye concentrations in a non-destructive way.

Typical techniques used in the photographic industry include densitometry and colorimetry. Densitometers measure the negative logarithm of reflectance and although they do not measure colour absorbance, properties of individual colourants

can be measured [139]. Colorimetry, on the other hand, refers to measurements of the physical quantities that characterise colours[1]. A colorimeter is, hence, an instrument used to measure the colour of light reflected or transmitted by a sample. They are often called tristimulus colorimeters [139] as they involve tristimulus integration (Figure 4.1).

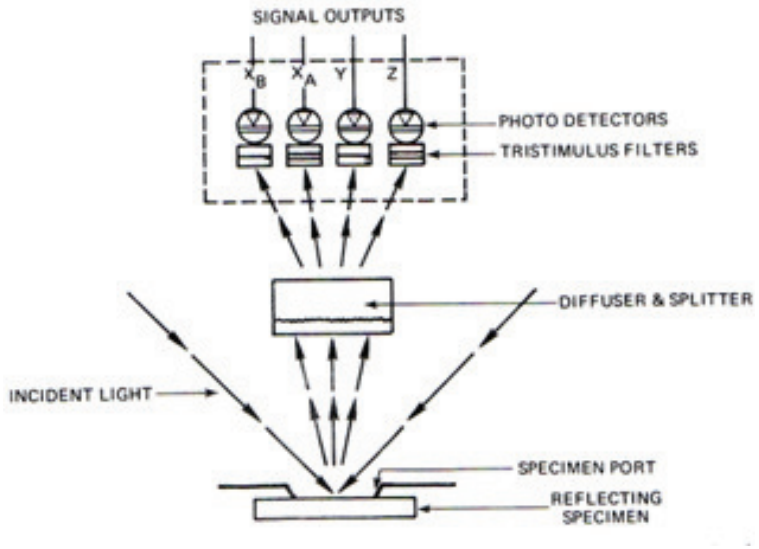


Figure 4.1: Block diagram of a tristimulus colorimeter.

Studies by Bernval'd et al. [140] have shown that while degradation of colour photographic images may be followed by either colorimetric or densitometric measurements, generally the colorimetric measurements are more compatible to what observers see, besides showing changes prior to densitometric measurements in colour photographs. Hence, colorimetry was prioritised as the method of choice. Colorimetry was particularly appropriate as photographic dyes are known to absorb in separate and distinct regions of the visible light spectrum[2] (Figure 4.2), and the number of dyes is also known to be limited in number in any one object.

[1]The first internationally agreed system of colour impression was the CIE (Commission Internationale de l'Eclairage) system published in 1931. In this and newer colour systems, each colour is described by a numerical value.

[2]Dyes are coloured due to the presence of chromophores. These are parts of molecules, generally composed of groups of multiple bonds, that absorb some of the light falling on them; if these systems are broken, the material would either shift colour or become colourless. The chromophoric systems of chromogenic dyes are optimised to absorb in specific regions of the visible light spectrum (Section 2.2.3.2)

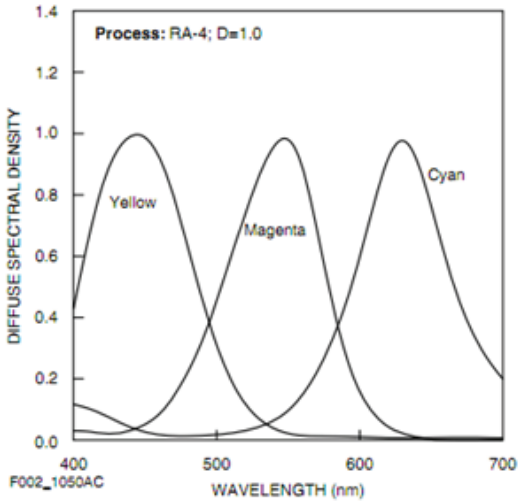


Figure 4.2: Curves showing the discrete absorbance of dyes in a typical chromogenic print [141].

4.1.1 Methodology

4.1.1.1 Samples

Samples for chromatographic analysis of 3 mm diameter were obtained from chromogenic prints listed in Table 4.1.

Table 4.1: Colour photographs investigated in this study.

Sample ID	Manufacturer	Backprint	Country	Year
AF28	Kodak	A Kodak Paper	Malta	1973
AF73	n/k	n/k	Malta	Late 1980s
AF92	Konica	Konica Longlife 100	Malta	Late 1980s
AF161	Kodak	Kodak Paper	India	2005
AF278	n/k	n/k	Malta	n/k
AF342	n/k	n/k	Malta	1998
AF419	kodak	Kodak Official Sponsors	Malta	1994
AF434	Fuji	FUJICOLOR Paper	Denmark	1998
AF444	Fuji	Fujicolor Crystal Archive Paper	Denmark	1998
AF521	AGFA	AGFA-Quality Paper	Slovenia	1987
AF566	n/k	n/k	Malta	Early 1980s

All of the photographs (except AF434, which was only used for method development) were also divided into 9 strips and placed at 80 ℃ for 4 weeks followed by another 4 weeks at 90 ℃ in dry air to provide a preliminary investigation of degra-

dation. The strips were then removed one at a time at one week intervals to give a sequentially degraded colour photograph (Figure 4.3). This provided degraded samples for further investigation.

Figure 4.3: Photograph AF28 sequentially degraded (from left to right) at 80 ℃ for 4 weeks followed by another 4 weeks at 90 ℃ in dry air.

4.1.1.2 Colorimetry

Reflectance spectra were measured using an X-Rite 530 SpectroDensitometer (D50/2° observation conditions, standard white background). All samples were measured prior to dye extraction and chromatographic analysis. sRGB (standard RGB colour model) values were calculated from the reflectance spectra (Appendix B).

4.1.1.3 Chromatographic Analysis

Ammonium acetate (HPLC grade) and trifluoroacetic acid (TFA, for UV-Vis spectroscopy, $\geq 99.0\%$) were purchased from Fluka (Milan, Italy). Methanol and ethanol were from Carlo Erba (Milan, Italy, pesticide analysis grade). Deionised water (Millipore, Billerica, MA) was used thoughout. All reagents and chemicals were used without any further purification.

For the extraction of dyes the samples were placed in 150 µL of 1:2 TFA:ethanol mixture for 5 min and shaken. After extraction, the solution was filtered under vacuum through a 0.45 μm membrane filter (Millipore, Watford, UK) and then dried under a stream of nitrogen until completely dry. The extract was then re-dissolved in 100 µL ethanol.

For chromatographic analysis, an HPLC system consisting of a PU-2089 Quaternary Gradient Pump with degasser (Jasco International, Japan), equipped with a 2-µL Rheodyne 7125 injection valve and coupled to a Diode Array Detector (DAD) MD 2010 (Jasco International) was used. The wavelength range of the detector was 200-600 nm, with 0.8 second sampling interval and 4 nm resolution. The signal was processed by ChromNav software (Jasco International). The chromatographic separations were performed using a C-18 column (Phenomenex Synergi 4u Fusion RP 80 A, 100 x 2 mm, Phenomenex), connected to a C-18 pre-column (1 mm Opti-Guard C18, Optimize Technologies, Oregon).

The elution gradient settings are provided in Table 4.2. A flow rate of 0.4 mL/min was used. Using this elution programme, all peaks of interest were suitably separated.

Table 4.2: Elution gradient used for chromatographic determination of dyes in photographic prints.

Time (min)	% 0.1 M Ammonium acetate (pH 6.2)	% Methanol
0	26	74
10	5	95
18	5	95
19	26	74
22	26	74

4.1.2 Results and Discussion

A non-destructive technique often needs to be calibrated against a reference technique and for quantitative analysis of dyes, chromatography is often used. For the analysis of chromogenic dyes, a method composed of an extraction and separation procedure had to be developed. The results are then compared to those obtained using the non-destructive method - colorimetry. These two aspects are discussed in the following sections.

4.1.2.1 Chromatographic Method Development

Dyes in chromogenic prints are found dispersed within a layer of gelatine. To enable their chromatographic analysis, they need to be first extracted into a solution. This is possible if gelatine is dispersed and the dye molecules dissolved by either achieving the point of zero charge (pzc) of gelatine[3], or by working at different pH values [143].

In the literature, various solvents have been suggested for the extraction of photographic dyes from photographic materials. An extraction method suggested for photographic negatives involved the use of dimethylsulfoxide (DMSO) [144]. DMSO is an important polar aprotic solvent for both polar and non-polar compounds and is miscible with a wide range of organic solvents and also water. However, DMSO is also known to broaden peaks in reversed-phase chromatography and also presents health risks [145].

Di Pietro [4] describes a method where ethanol is used to extract dyes from a chromogenic film, while the solution is heated and agitated. An addition of diethyl ethanol has been suggested as it is a better solvent. However, ethanol was found to be too volatile to allow for prolonged heating.

Bristow and Bumfrey [138] used methanol and acetonitrile as the main components, with small amounts of water and acetic acid (9% water, 6% acetic acid, 25% acetonitrile and 60% methanol). The dyes were extracted by sonication for 30 minutes. In this paper an HPLC methodology is also proposed. This has, therefore, been used as a starting point in this work. However, the extraction solvent specified in Bristow and Bumfrey [138] did not lead to satisfactory extraction even after 2 hours of ultrasonication at 60 ℃ and the method had to be optimised.

To try to find the optimal pH of the solution approaching the pzc, differently concentrated solutions of HCl and KOH were investigated. The extracts were analysed using Flow injection analysis (FIA)[4]. It was determined that acidic conditions were the most appropriate. While a mixture of 100 µL proved to be too acidic, the addition of 20 µL 30% HCl appeared to be appropriate as peaks were observed for components absorbing at 650 nm (cyan) and 550 nm (magenta). DMSO was also investigated, but it proved to be less efficient than this extraction solution.

[3]Typically, gelatine used in photographic materials has low molecular weight, and hence a low pzc as high-pzc Ag-halide peptizers can lead to sensitised flocculation rather than peptization under many precipitation conditions. Typical pzc is between pH 5.5 and 6.5 [142].

[4]Flow injection analysis was carried out using the same set up as for chromatography without the chromatographic column.

However, no peaks were observed at ∼440 nm (yellow; Figure 4.4). Weaker acids were considered, particularly TFA (trifluoroacetic acid), and ethanol was also investigated. On analysing the extracts using both ethanol and the extraction solution proposed by Bristow and Bumfrey [138] with different concentrations of TFA in the place of acetic acid it was observed that while the extracts according to Bristow and Bumfrey lacked a component absorbing at ∼440 nm as in previous investigations, those obtained using ethanol, particularly with higher concentrations of TFA (1:2 and 1:1 TFA:ethanol solutions) did contain the yellow dye (Figure 4.5). The best extraction solvent was identified to be 1:2 TFA:ethanol as it extracted the dyes without disrupting the chromophoric systems.

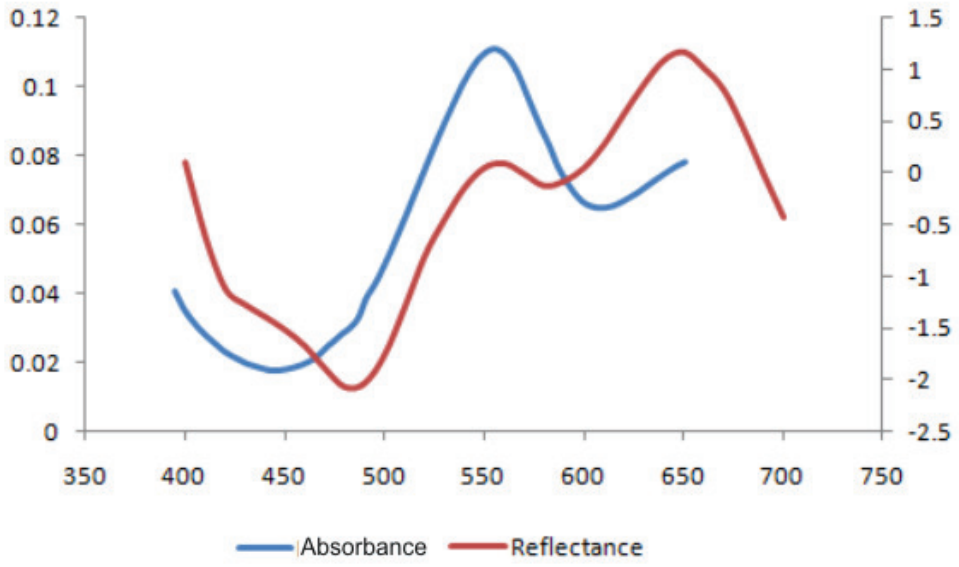


Figure 4.4: Comparison of the reflectance spectra obtained using a spectrodensitometer and of absorbance spectra obtained using FIA. The dyes were extracted using a 1:2 TFA:ethanol solution.

Once a satisfactory extraction procedure was developed, as shown by comparison of spectra from colorimetry and flow injection analysis, a method for the separation of dyes in a chromatographic column was required. The elution gradient as proposed by Bristow and Bumfrey [138] was used as a starting point and was slightly modified to give an optimised elution gradient as outlined in Section 4.1.1.3.

A comparison of the retention times of the dyes was then performed on the 10 photographs investigated (Table 4.3). As expected there was a limited number of

dyes present in each layer, in most cases one or, two dyes at most. In instances where there were two one of the dyes was much more abundant than the other, as is the case of the two cyan dyes in Figures 4.5 and 4.6. Also, since these samples were authentic it was expected that some of the peaks were possibly degradation products.

Table 4.3: Table of retention times of dyes extracted from the ten authentic colour photographs.

	Sample/retention time (min)									
Abs max	AF28	AF73	AF92	AF161	AF278	AF342	AF419	AF444	AF521	AF566
440nm	13.2	11.3	13.2	17.3	13.3	11.0	15.1	13.4	13.1	13.5
(yellow)	11.5			16.4		14.4				
550nm	16.1	13.4	14.1	13.4	9.7	14.5	13.4	14.3	14.6	15.0
(magenta)	14.5			14.3						
650nm	14.4	13.1	13.2	12.4	10.3	13.6	11.9	15.6	15.0	14.4
(cyan)		13.4	14.4	13.2	14.1			15.2		

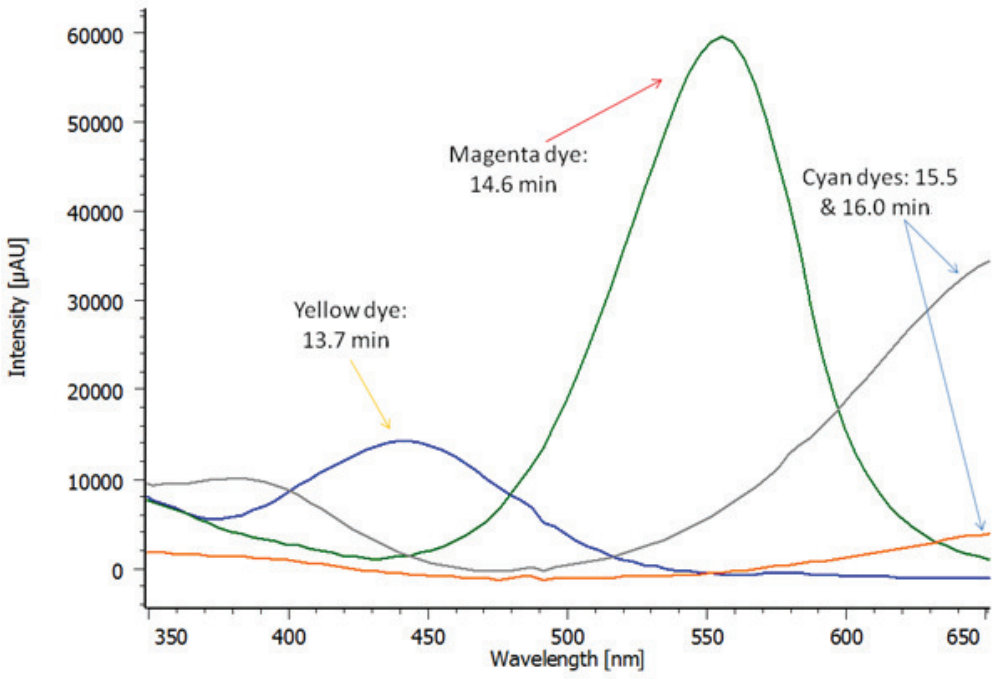


Figure 4.5: Spectra of chromatographic peaks of compounds extracted from AF434, obtained using 1:2 TFA:ethanol solution. The yellow dye eluted at 13.7 min, the magenta dyes at 14.6 min, and the two cyan dyes at 15.5 and 16 min.

As can be seen in the chromatogram at 264 nm (Figure 4.6), UV-absorbing components were also observed. These components (Figure 4.7) could consist of couplers

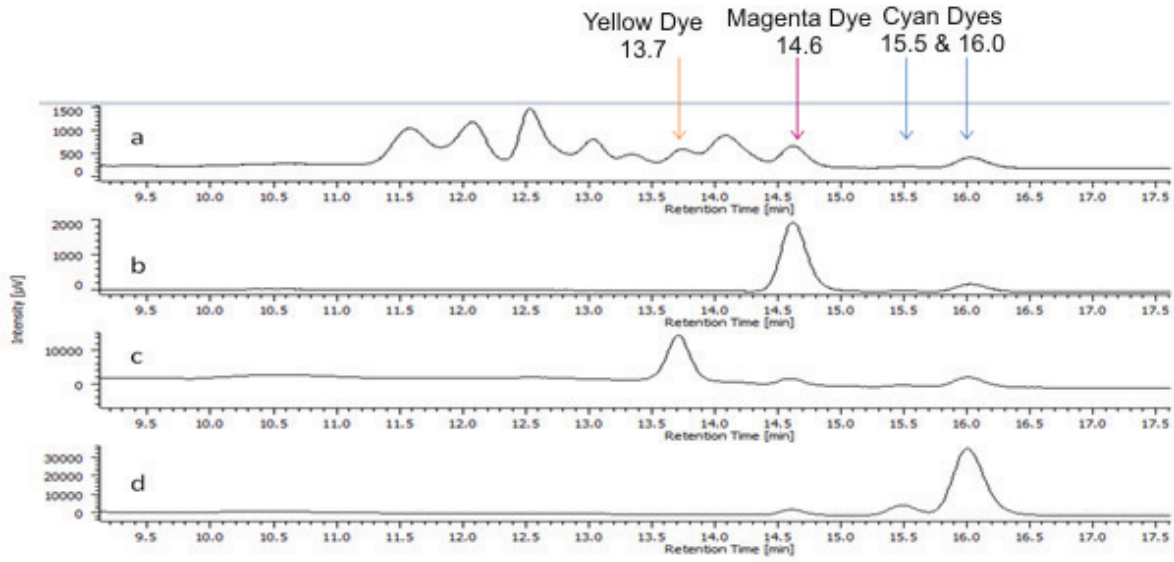


Figure 4.6: Chromatograms of a brown area from the photograph AF434; a: detection at 264 nm, b: 550 nm, c: 440 nm and d. 650 nm. The yellow dye eluted at 13.7 min, the magenta dyes at 14.6 min, and the two cyan dyes at 15.5 and 16 min.

(undeveloped dyes) and other components added to the photographic emulsion. As they do not absorb in the visible part of the spectrum they are not expected to affect the visual appearance of photographs. Therefore, they were not of interest to this research

4.1.2.2 Comparison of Chromatographic and Colorimetric Data

If reference compounds were available, the chromatographic method could be used for quantitative analysis. Otherwise, reference compounds could be obtained by extraction and preparative chromatography of individual dyes from a large number of identical photographs. To avoid this, changes in colour were evaluated colorimetrically and normalised to the initial dye (cyan, magenta, yellow) intensity. However, to use this approach it had to be ascertained that spectra of extracted dyes correspond to the reflectance spectra as measured on the same photographic samples. Hence, the reflection spectra were compared to the spectra of dyes obtained using HPLC-DAD, extracted from the same individual sample.

The absorption spectra of the dye compounds obtained chromatographically are shown in Figure 4.8. The spectra of individual dyes are also summed up to give

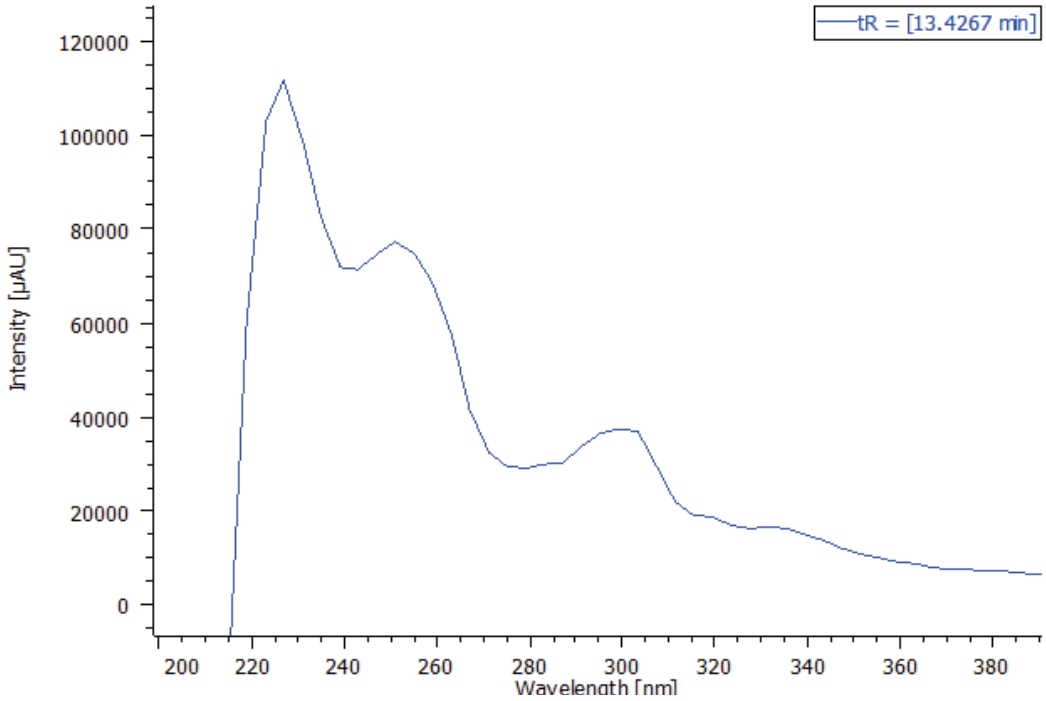


Figure 4.7: The spectrum of a UV-absorbing compound from the sample AF581 (white area). tR = retention time.

the 'Sum spectrum' of the dyes in solution. This was done for comparison with the reflectance spectrum, converted into an absorbance spectrum using the Kubelka-Munk equation:

$$A = \frac{1-R^2}{2R}$$

where A is the absorbance value and R is the reflectance value.

The sum spectrum of dyes in solution is evidently trimodal, not dissimilar to the reflectance spectrum obtained colorimetrically, despite the considerable, but consistent shift in peak maxima. This shift is probably due to solvation-related shifts [146], as the colorimetric spectra were obtained in the dry state, while the chromatograms were obtained in solution. This finding, although not surprising, is important as it justified the use of changes in reflectance spectra for quantitative evaluation of the rate of degradation of individual dyes.

Furthermore, the cyan, magenta and yellow (CMY) dyes are complementary to the red, green and blue (RGB) of the sRGB colour model, respectively (Figure 2.4) [23]. Thus, it is expected that by following changes in the sRGB colour coordinate

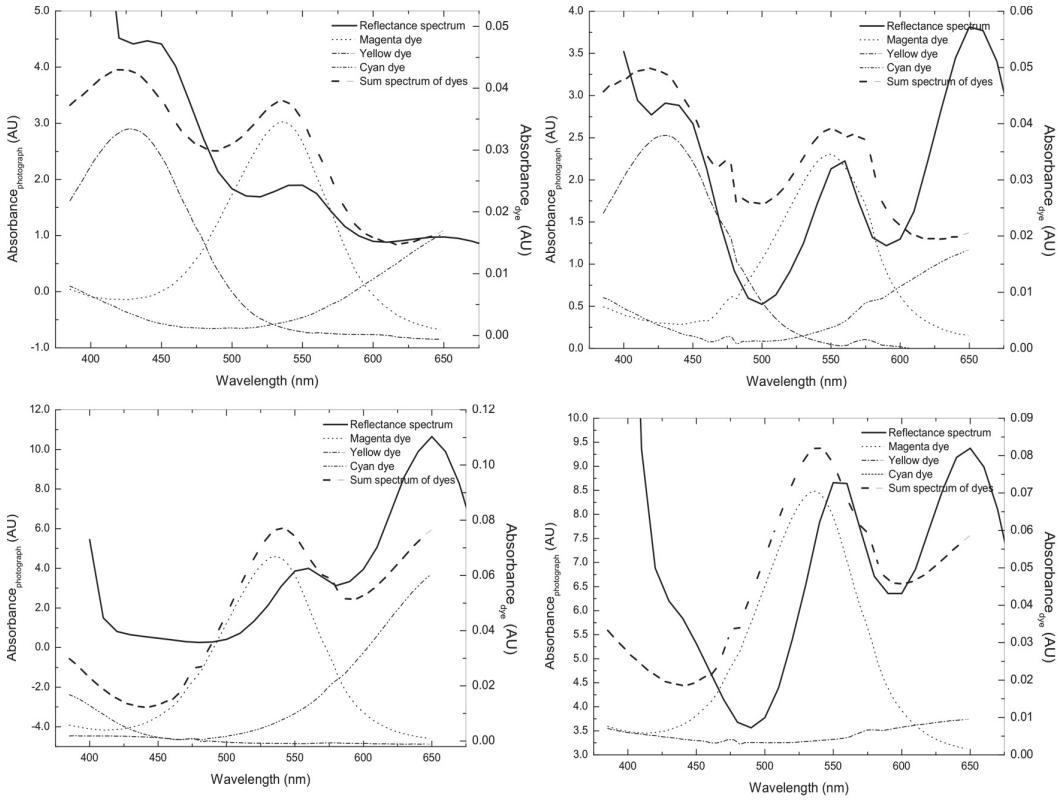


Figure 4.8: Comparison of the reflectance spectra of four sample photographs, and of the individual dyes (and their sum) as extracted from the same 3-mm sample area. After extraction, chromatography was performed with diode-array detection enabling the individual dye spectra to be obtained. A: Konica, 2006; B: Fujifilm, 1998; C: Konica, 2006; D: unknown, 1980s.

system it would be possible to monitor changes in dye concentrations. The sRGB model numerically represents an absolute colour space in terms of three coordinates: red, green and blue [147]. In fact, a paired samples t-test comparing the sRGB colour system and the corresponding expected dye absorption maxima values indicated that the two systems are statistically identical ($p > 0.05$). Thus, the sRGB system was selected to describe changes in dye concentrations, expressed relatively to the sRGB values at $t = 0$ (before a degradation experiment) as it is a standardised system, correlates with the absorption maxima of dyes, and with colour chromaticity.

4.2 Dating of Photographs

Dating of artefacts and historic objects is a complex interdisciplinary area of research. Often, the most informative (if not the only) indication of the date of manufacture of a photograph is the period of time during which a particular process was popular [2]. However, each process could have been used in different parts of the world and by different photographers at varying time periods. Also, as seen in Figure 4.9, during any one time a number of processes would have been in use.

However, this relatively rapid changeover of photographic processes was dissimilar to the case of gelatine silver and chromogenic prints. Chromogenic prints have now been around for decades with one of the few significant changes being the switch from fibre-based supports to resin-coated supports in the early 1970s [25, 31, 35–37].

Besides process, other indications of the age of a photograph are sometimes considered. By historic image analysis, such as on the basis of clothing style, license plates, and the presence or absence of other features such as television sets, dating may be possible [2]. However, this does not help if the relevant information is not present, or where the object is a copy.

Therefore, most current methods for dating photographic prints either rely on considerable technical knowledge, or on the chance presence of a feature in the image. However, more often than not either one or the other (or both) are unavailable. Therefore, a new, ideally non-destructive and portable dating tool, based on material properties that does not require considerable technical knowledge by the user would be advantageous. In combination with chemometric data analysis, near infrared (NIR) spectroscopy has already been shown to be useful for dating of historic paper [148]. This method was investigated for dating of chromogenic prints in this study.

NIR spectroscopy uses the region of the electromagnetic spectrum from ∼780 nm to ∼2500 nm for analysis. It is becoming a widely popular technique due to its speed, accuracy, and diverse applicability, finding applications in the agricultural, chemical, pharmaceutical and textile industries, amongst others [149]. Another benefit, particularly relevant in heritage science, is the fact that it is non-destructive. It often involves no sample preparation, making it easy to use, also by non-professionals. Furthermore, it is useful for detection of low concentrations of analytes (∼0.1%) if the analyte contains suitable chemical structures [150].

An advantage of NIR spectra is that, though complex, they are rich in infor-

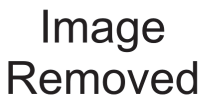


Figure 4.9: Chronology of photographic processes. The dates represent approximate dates of use in the US rather than invention or discovery. The thickness of line indicates relative use [25].

mation as they contain a large number of combination bands, as well as overtone peaks, giving rise to their complexity [151, 152]. The predominant near-infrared spectral features include X-H stretching vibrations. The methyl C-H, methylene C-H, aromatic C-H, and O-H stretching vibrations tend to be reflected in the major peaks, while methoxy C-H, carbonyl-associated C-H stretching, N-H from primary amides, secondary amides (both alkyl, and aryl group associations), N-H from primary, secondary, and tertiary amines, and N-H from amine salts provide minor but still important peaks (Figure 4.10) [151, 153]. These absorptions occur at considerably lower wavelengths (higher frequencies) than the fundamental absorption bands [151].

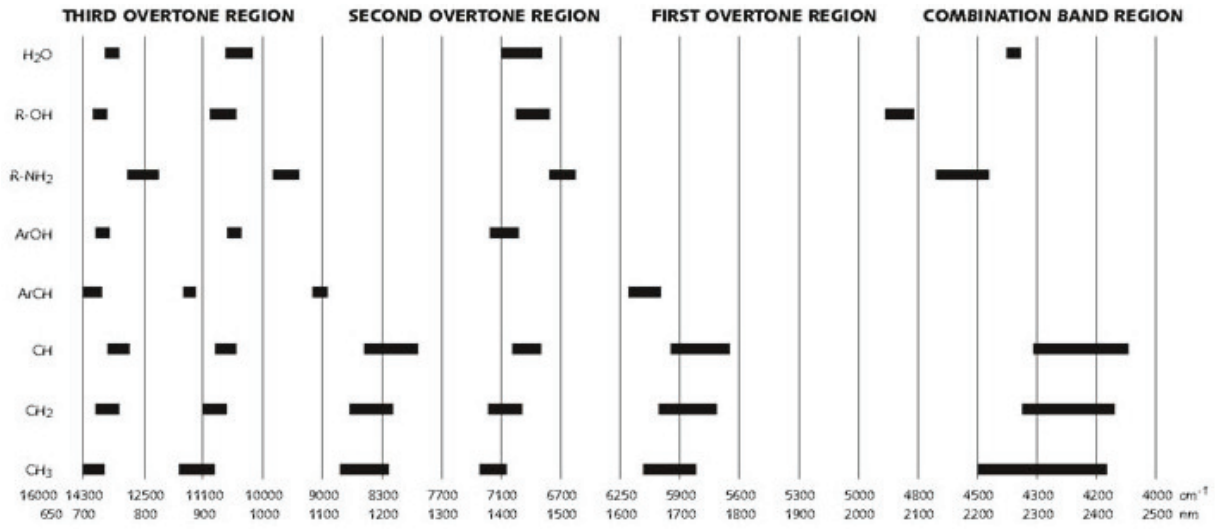


Figure 4.10: Chart of characteristic NIR bands [154].

Combination peaks arise when overtones of two or more vibrations combine into one band (through the addition or subtraction of energy) [150]. Fermi resonance is another feature, occurring when an overtone or combination band interacts strongly with a fundamental peak due to vibrations of the same symmetry at similar unperturbed frequencies. However, due to the Franck-Condon principle, which gives rise to anharmonicity, the overtone and combination bands do not appear at exact multiples of the fundamentals. Hydrogen bonding in particular, is known to exert a large effect on peak position. Due to its small size, it causes significant deviations from harmonic oscillations [150, 151, 155].

As most of these transitions are quantum mechanically forbidden, NIR bands

tend to be 10-1000 times weaker than the fundamental bands [150, 151]. This has its own advantages as NIR radiation typically penetrates much farther into a sample than radiation from other parts of the infrared region of the electromagnetic spectrum. This makes it very useful for probing bulk material properties without the necessity of sample preparation [152]. NIR radiation, in fact, typically penetrates 1 - 4 mm in the reflectance mode[5] (depending on the wavelength and matrix) [150], and chromogenic prints, as discussed in Chapter 2, are typically 250 µm thick [39]

However, the complexity of spectra means that they do not lend themselves to an analytical approach easily. Therefore, development of NIR applications is almost entirely dependent on statistical and chemometric methods, involving a significant amount of preparatory work [150]. Thus, NIR spectroscopy gained wide acceptance only as the computing power of personal computers increased.

To extract useful data from NIR spectra multivariate data analysis is most often used [150]. This represents a set of techniques used for the analysis of data sets with more than one variable [156], e.g. the multitude of data points in an NIR spectrum. They allow for the representation of an n-dimensional data structure into a smaller number of dimensions [157].

In particular, partial least-squares regression (PLS) is typically used with NIR spectra. In this method, complex multivariate analysis problems are solved by a sequence of simple least squares regressions using an iterative approach [150]. The best model is then determined on the basis of a comparison of root mean square error of cross validation (RMSECV) values for different spectral smoothing and pathlength correction pre-treatments.

NIR spectrosocpy in combination with multivariate analysis (MVA) was thus identified as the method of choice for the development of a dating method. A selection covering the range of variety of chromogenic prints was analysed. This allowed for a model to be built that can then predict the date of unknown samples.

[5]While the radiation might penetrate, it is not necessary that information will be reflected back. In paper, information is obtained only from around 500 µm [148]

4.2.1 Methodology

4.2.1.1 Samples

159 prints were selected from the research collection of colour photographs discussed in Section 2.3 with dates of development covering the period 1942-2008. The prints were selected so that as many manufacturers and countries of production as possible were included.

4.2.1.2 NIR Spectroscopy

NIR spectra (50 scans/spectrum) were obtained on two locations on the *verso*[6] of the colour photographs (Phazir, Polychromix). The two spectra were then averaged. Data was obtained in the wavelength range 1595-2400 nm.

4.2.1.3 Chemometric Analysis

The samples were divided into a calibration set (109 prints = 2/3 of prints) and a validation set (50 photographs = 1/3 of prints). The samples were distributed into these two sets at random.

Partial least squares regression (PLS) was used to build the dating model using Polychromix Method Generator Application version 3.101 (Polychromix). Optimal correlation was obtained by optimising the spectral pre-treatment methods.

4.2.2 Results and Discussion

NIR spectroscopy is rapidly becoming one of the most popular techniques for non-destructive characterisation of heritage materials due to its speed, accuracy and versatility. Differences between NIR spectra of similar materials are not easily visually observable; in the case of colour photographs, the main easily visible difference is between paper-based and resin-coated prints (Figure 4.11). Thus, chemometric methods are required to extract the relevant information [148].

To build a PLS calibration, the spectra are divided into two sets: a calibration, or training, set containing $\frac{2}{3}$ of the spectra, which is used to build the calibration, and ideally a validation set containing the other $\frac{1}{3}$, which is used to validate the calibration. For the model to be valid it is essential that the calibration set, as a

[6]Back side of the print.

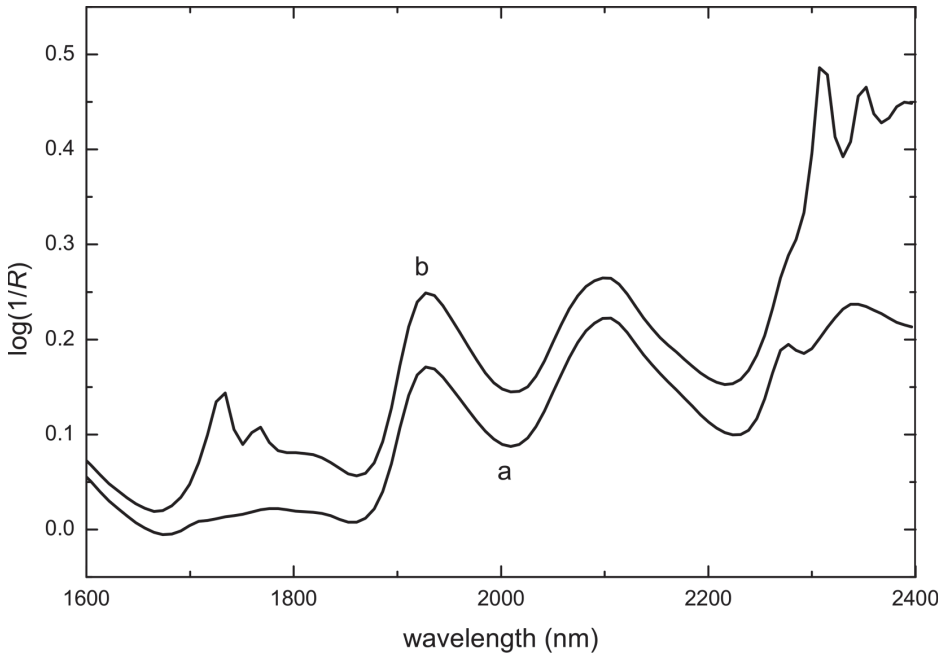


Figure 4.11: Typical NIR spectra (1600 - 2400 nm) of a paper-based (a) and a resin-coated (b) photographic print.

group, is representative of the unknown samples on which the analysis will be used [158]. Hence, chromogenic prints covering the whole range of prints in the collection from 1942 to the present, and including a variety of manufacturers and countries of production, were selected for this study from the research collection.

Spectra were taken on the *verso* side of the prints as the gelatine in the emulsion layer overshadowed the spectral data when spectra were taken on the *recto*[7] side. This is important as it can be expected that the support composition changed most often over the years, as components such as optical brightening agents and pigments were added and optimised.

Once the spectra were obtained, partial least-squares regression (PLS) was carried out. The pathlength correction used was the standard normal variate (SNV) transformation. This correction is often used for reflection spectra. The mean of each spectrum is subtracted from each value, and is then normalised by dividing by the standard deviation of the same spectrum [159]. The SNV transformation is often found to improve calibration by reducing the effects of shifting baselines caused by scattering [160].

[7]Side bearing the image; front.

The optimal model was found to be the combination of SNV with a Savitzky-Golay 3-point 2^{nd}-order derivative smoothing. Savitzky-Golay smoothing works by weighting the raw data points by the application of a polynomial function to the data within the filter window. This typically preserves data features such as peak height better than other filters such as moving average filters [161]. In particular, the second derivative, which was used in this case, is known to have a pronounced minimum at peak maximum, which is suitable for the evaluation of peak position. Also, compared to the original signal, the full-width-at-half-maximum is smaller for the peak in the second derivative, so it can distinguish between peaks not recognised in the original signal [162].

The developed model (Table 4.4, Figure 4.12) shows a very satisfactory correlation between the predicted and actual date of development of chromogenic prints. Considering the inherent uncertainty due to the time difference between photographic paper production and development (that can be up to a few years), and the fact that each material was produced for a number of years, the RMSECV in Table 4.4 can be considered as highly satisfactory. On validating the model (Figure 4.13), the root mean square error of prediction (RMSEP) was very similar to the RMSECV obtained for model calibration (Table 4.4). This indicated that the model is adequate for predicting the date of unknown samples.

Table 4.4: PLS cross-validation and prediction model data for determination of the year of development of chromogenic colour prints.

		Cross-Validation		Prediction	
Measured property	Range	RMSECV	R	RMSEP	R
Year of development	1942-2008	5.4 years	0.9592	5.5 years	0.9547

4.3 Conclusion

Materials research is a broad area of science dealing with the study and characterisation of materials. In the field of heritage science this area of research is often concerned with the development of potentially non-destructive methods of materials characterisation and with studies of materials stability.

Development of a non-destructive method for monitoring dye concentrations was important for the analysis of photographs during long-term accelerated degradation

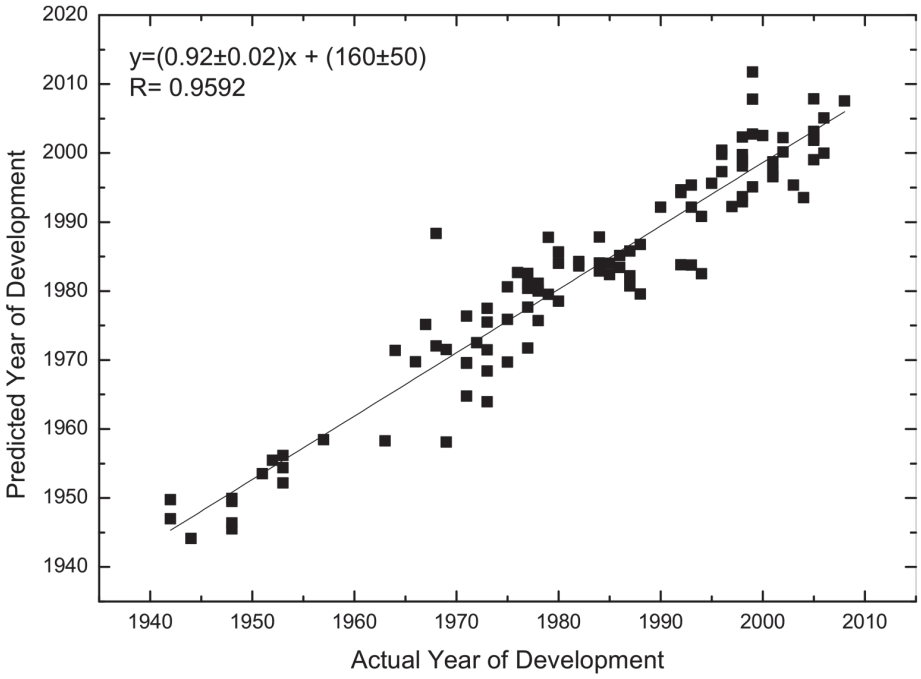


Figure 4.12: PLS cross validation for determination of the year of development of chromogenic prints.

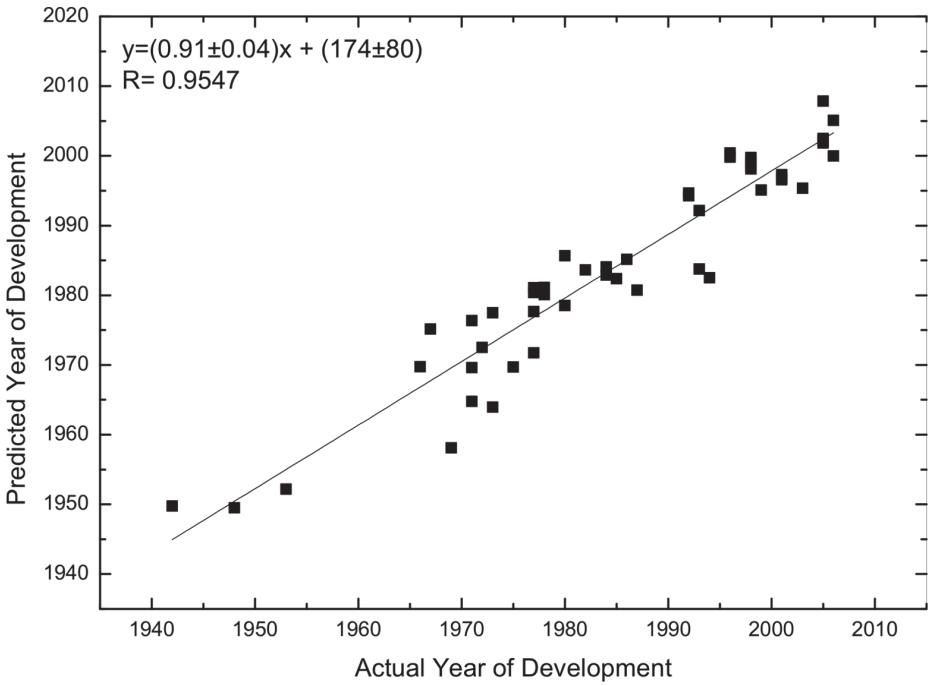


Figure 4.13: PLS validation for determination of the year of development of chromogenic prints.

studies. A methodology was developed to investigate the concentration of dyes in chromogenic prints using chromatography and the results were compared with colorimetry. Since colorimetric measurements are directly related to the concentration of dyes in chromogenic prints, RGB coordinates from the reflection spectra of photographs can be used to evaluate the rates of change of dye concentrations during degradation. Colorimetry was found to be applicable as the measurements can be correlated with psychophysical descriptions of colours, i.e. the values it provides directly relate to what the observer experiences.

Further materials research led to the development of a non-destructive dating method based on NIR spectroscopy. Identification of the age of prints is often performed based on expert knowledge and destructive testing. Simpler spectroscopic methods could potentially be used by non-specialist staff, thus making dating accessible for curatorial research to a wide range of institutions. The dating model is useful when the year of development is in contention, or when this information is relevant to understanding of the preservation needs of specific materials.

Having shown the strength of NIR spectroscopy in combination with multivariate analysis for dating, it is evident that the technique could be more widely exploited for the characterisation of chromogenic prints and it was also investigated for the prediction of print stability. This research will be discussed in Chapter 7.

Chapter 5

Values Research

The third line of research related to the lifetime of chromogenic prints is values research. Values are central to heritage. However, as yet, most studies have tended to focus on qualitative assessment of heritage values or quantitative assessment of economic value, rather than on quantitative assessment investigating the relationships between material and value change.

This chapter briefly examines the concept of value in heritage studies. This is followed by a discussion of the methodology designed in this work to determine the change considered to be unacceptable for a chromogenic print in an archival collection. Finally, the results obtained during stakeholder workshops carried out to determine unacceptable change, hence, damage, will be discussed.

5.1 Values and Heritage

The Oxford English Dictionary [163] defines 'value' as 'the relative status of a thing, or the estimate in which it is held, according to its real or supposed worth, usefulness, or importance' [163]. Therefore, value refers to the conferring of meaning and worth to objects; 'value' is what 'converts' objects to 'heritage', although not all value assignment results in heritage status [164]. It is, therefore, impossible to ignore the role of values if a holistic assessment of cultural heritage material change is attempted.

Objects are typically valued as heritage due to a function they have in a society. This can be an aesthetic function, an evidential or a utility function, amongst others. Determining heritage values is, therefore, a conscious process of, first and foremost,

understanding the purpose of the object. Often, a limited number of stakeholders, be it individuals or institutions, impart their values to a heritage object based on their social contexts and processes [164–166].

However, an issue arises in that the value of an object may only be relevant in the context of the stakeholders who assigned value to the object and the purpose it is thought to fulfil [167]. Nevertheless, assessing heritage values is essential since values are at the heart of our understanding and interaction with heritage objects. Therefore, besides physical characterisation and management of material change, another challenge involved in heritage research is understanding why and how heritage is valued [164, 168].

In recent years, interest in methods for assessing and monitoring values in cultural heritage has increased [90, 164, 165, 169]. However, even though values are important in heritage research, shaping and informing the field to a large extent, methods for their quantitative assessment, besides for economic value, are pronouncedly missing. This is particularly true for methodologies that can be correlated with observations of material change as this requires investigating how material properties of an object affect its intangible properties. This is problematic as questions of value are not easily susceptible to quantitative solutions [90, 169]. However, it is becoming increasingly necessary to quantify aspects of value.

The lack of value assessment methodologies in heritage studies makes it necessary to look for methodologies available in other domains of research [165]. In general, two main classes of methods, those suited to cultural and those suited to economic values, have been identified and applied in the heritage field [165, 169].

5.1.1 Anthropological/Ethnographical Approach

The anthropological/ethnographical approach is the traditional approach for heritage value assessment. Generally, expert analysis is used to determine the relevance of values. This methodology is criticised as it leads to the interpretation of values internal to the profession rather than their interpretation within a wider context [169, 170]. The second general approach is the ethnographical approach where values are elicited, generally in a qualitative manner, through a description of cultural characteristics [169].

These methods are typically used to elicit the values associated with an object or system. The key problem with these two approaches in the context of this work is

that they rely too heavily on qualitative analysis, which does not lend itself well for integration with the quantitative approach of physical methods. Hence, difficulties arise if correlation between values assessed in this manner and quantitative material assessment is attempted for predictive purposes, as was the aim in this project.

5.1.2 Economic Approach

Economic methods have gained a great deal of credibility as they measure value in what appears to be an objective manner. As they deal with monetary value, they appeal very effectively to the increasingly business-directed mentality of society [169, 171]. Two general methodologies are used: revealed-preference methods, where data from existing markets for heritage-related goods and services are analysed, and stated-preference methods, where hypothetical markets are created for survey respondents to make hypothetical choices that are then analysed as value judgements [169].

The various tools adapted for cultural heritage value assessment tend to be adapted from those devised to measure the value of environmental resources as part of environmental conservation decisions [169]. These economic tools seem to be the most developed and widely accepted value measurement tools and, for a long time, were considered to be the most appropriate in the heritage field. However, doubts have arisen as to whether they are as accurate in measuring cultural values as has been thought in the past [165]. This has led to a move away from the monetary approach, particularly as it is often acknowledged that values in cultural heritage go beyond the financial [172]. Hence, economic value is not able to adequately reflect the multitude of values attached to heritage. Therefore, though economic valuation might often be useful, it is not always the most appropriate.

5.1.3 Overview

There are various motivations for valuation of heritage, each with its own approach. These different approaches to valuation may lead to different outcomes for heritage preservation [164].

The two approaches discussed above represent two greatly different perspectives of looking at heritage values, with the cultural value methods often being qualitative and economic methods representing quantitative methods. Both methods rely

heavily on respondent answers. This is particularly relevant as, in recent years, there has been increased interest in public participation in the assessment of value [172, 173]. However, as clearly stated by Satterfield [172], as values are typically not clearly set out in respondents' minds, methodologies centred on human attitudes and preferences may be vulnerable to manipulation. There, therefore, is a need for methods that limit this possibility of manipulation.

In such exercises, it is typical for valuation questions to be simplified to their component parts to allow for participants to focus on the decision being investigated within the task. Hence, in this project, the question to be investigated was distilled down to what was of greatest interest in the context of this project and an approach where valuation is the result of individual preferences was selected as the methodology of choice.

5.2 End-of-Lifetime of Chromogenic Prints

In this study, photographs as cultural heritage objects were investigated. Their unique history, during which colour was absent for the first ninety years for purely technical reasons, resulted in visually distorted monochromatic images [174]. Such deprivation of reality is difficult to imagine in other forms of visual impression, such as painting. All this makes the understanding of the specific contexts of values a highly interesting area of research.

As discussed earlier, an object is considered to be 'heritage' based on the value society places on the object. Therefore, one can consider that once an object, for whatever reason, loses its value, its lifetime with respect to that particular value is expended. Having developed methodologies for monitoring material changes in chromogenic prints (Chapter 4), it is now essential to identify what degree of material change constitutes an unacceptable change in the value of an object. For this reason, the value of greatest interest for colour photographs had to be identified, and an appropriate way of assessing the value had to be determined.

A previous study by Bülow [10], on the value of records at TNA, identified informational, material and cultural values as the values of greatest interest to archival users. Of these, informational value, i.e. the written or recorded information, was by far the most important (Table 5.1). This is also very well aligned with the stated TNA priority to "guarantee the survival of today's information for tomorrow" [9].

Hence, informational value was identified as the value of interest for this project.

Table 5.1: Assigned value of records at TNA [10].

	Assigned Values		
Assessment Unit	Informational	Material	Cultural
Paper and parchment	50%	20%	30%
Microfilm (archival masters)	80%	10%	10%

Information within a photographic print, however, encompasses a variety of its aspects. It lies in the technology used to produce such a print, the place the print was manufactured and the photographer, amongst others. However, the information most likely to be considered is that present within the image itself. As we have learnt in Chapter 2, in spite of technological advances, image degradation still remains a major issue in the conservation of chromogenic prints, leading to this information being the value aspect most likely to be lost.

Having identified the value aspect of chromogenic prints that is most relevant, a methodology for the fitness of objects to maintain this value and, hence, to fulfil this purpose had to be identified. The two value assessment methodologies discussed in the introductory section were investigated initially. However, it was immediately clear that, while anthropological/ethnographic methods are appropriate for the identification of values, they are not appropriate to measure changes in these values as these methods are typically qualitative. Economic values were also not considered appropriate as, while these methods are suitable for assessing changes in economic value reflecting the values stakeholders can evaluate in monetary terms, they do not lend themselves well to assessing changes in other values, such as utility value, including informational value.

For this reason, as is often the case in cultural heritage research and especially within values research, assessment methodologies used in other fields were investigated for measuring the fitness-for-purpose of photographs in terms of the informational value of an image. As discussed earlier, stakeholder input into such value assessments is appropriate. As the customers of the photographic industry are the users of their products, there have been numerous studies and methodologies developed using users as the meter. Most of these studies have used psychophysical methodologies [175]. Hence, these methods were investigated.

As Baird and Noma [176] clearly define, psychophysics is "the quantitative

branch of the study of perception, examining the relations between observed stimuli and responses and the reasons for those relations". It allows for a quantitative relation to be extracted, while providing a reason for it [176]. Though psychophysics is considered to be a field within psychology, it has been applied widely in other fields of research, from occupational and clinical health [177, 178] to politics and law [179]. As has just been indicated, pyschophysical methods are also well established for understanding image quality and its effect on viewers [180–182]. British standards have also been published for estimating different aspects of image quality using this technique [183–185].

Psychophysical studies are broadly divided into two main classes. Threshold methods are based on the energy a user can just barely detect, such as the decibel level at which sound can be heard. These methods are used when detection of a stimulus is the factor of interest. Supra-threshold methods are used in instances where the stimuli are all easy to perceive and are used to discriminate between stimuli, such as discrimination between sounds [186].

Most work on acceptable colour changes has so far focussed on the use of threshold methods and the concept of 'just noticeable difference' (JND). JND represents "a stimulus difference that leads to a 75:25 proportion of responses in a paired comparison task" [183]. This concept is not only used for colour changes but also for all aspects of image quality e.g. blurring and contrast, as well as other aspects apart from image quality [187].

In the heritage field, this concept (including synonymous terms such as 'just perceptible colour difference') has mainly been used to understand the effect of illumination [188–191]. Having determined what a JND or perceptible change is, a timeframe in which this can occur can be determined [192]. However, problems have been identified in that, though values have been proposed, the magnitude of a 'just noticeable' difference is not clearly defined [188], with other ratios of stimulus recognition, such as 50:50, also being used.

However, the concept of a JND is better suited to measure visual ability rather than the perception of change in an image by a viewer [193]. These concepts might work well for materials that are not expected to change much as, in such cases, it might be more reasonably proposed that any change is unacceptable. However, photographic dyes are inherently unstable, making such propositions impractical.

Therefore, concepts that go beyond JND need to be explored, such as 'unac-

ceptable change'. This is also more suited to the needs of this project. Hence, a supra-threshold approach using scaling methods was chosen. These methods are generally classified into three:

- Partition of the sensory continuum into equal intervals: Category scaling;
- Ordinal discrimination judgement of stimuli: Comparative methods;
- Expression of perceived magnitudes of stimuli: Magnitude estimation.

In category scaling, the goal is to assign numbers to perceptual events. The benefits of category scaling is that it allows for direct observer response to changes, though it is then restricted to only a number of categories [186]. Nevertheless, category scaling methodologies exhibit high stability and lead to low participant stress when compared to other methodologies [183]. This was considered the most suitable method to adopt, using category titles as prescribed in the experimental procedure in BS ISO 20462-2:2005 [184].

This approach was chosen due to its clear suitability to the study of perception of photographic materials, as well as its fitness to answer the questions being asked within this study. The method allowed for the perception of participants to be determined with regards to unacceptable changes. Therefore, the remainder of this Chapter presents the methodology developed to determine the 'Unacceptability Threshold'[1] for a chromogenic print with regards to safeguarding the information.

A psychophysical methodology has been followed. An assessment workshop was designed and carried out during which participants were asked to classify a series of degraded chromogenic prints images according to the acceptability of image changes. The data collected in these workshops allowed for the ΔE_{RGB} at which a range of different photographs were judged to be unacceptable to be determined. ΔE_{RGB} is defined as:

$$\Delta E_{RGB} = \sqrt[2]{\left(1 - \frac{R_t}{R_0}\right)^2 + \left(1 - \frac{G_t}{G_0}\right)^2 + \left(1 - \frac{B_t}{B_0}\right)^2}$$

where ΔE_{RGB} is the total colour change in terms of RGB; R_0, G_0 and B_0 are RGB values of the original images; and R_t, G_t and B_t are RGB values of the degraded images.

[1] In this discussion, the term 'Unacceptability Threshold' refers to the ΔE_{RGB} that was classified as unacceptable.

As may be expected, the perception of an observer as to what this constitutes may depend on a number of factors, such as previous experience with such an assessment, content of photograph or lighting conditions in assessment room. Therefore, investigations as to whether this varies with respect to the assessor, content and characteristics of the photograph were also carried out. Hence, prior to determining the degree of change that would constitute the end-of-lifetime[2], a better understanding of data collected during assessment workshops, as described in the following paragraphs, was essential.

5.2.1 Methodology

5.2.1.1 Image Preparation

A series of images were selected for investigation in this study. The selected photos varied along key parameters, such as fading profile[3], content type[4] and level of detail[5] in order to investigate the effects of these characteristics on Unacceptability Threshold and in order to be able to generalise from the results.

The fading profile of two photos from the research collection discussed in Section 2.3, AF541 and AF419, were investigated as, while AF419 exhibited selective fading[6] (Table 5.3), AF541 exhibited more equivalent fading[7] (Table 5.2) on accelerated degradation. This was determined following visual analysis of the images in Adobe® Photoshop®.

The selected images represented three content classes (technical, landscape and people), with five photos per class (15 in total; Figure 5.1). These represent types of images that are most commonly found in archives as observed during a search through TNA's collection.

The photos were then digitally degraded using Adobe® Photoshop® following the degradation profiles. A description of the photographs and their characteristics are shown in Table 5.4. The photo number and number of pieces (i.e. number

[2]The end-of-lifetime is defined for this project as 'the point in time to which the informational value currently present in an object survives'.

[3]Do the three dyes change at similar rates [non-selective fading], or does one dye degrade at a much faster rate than the others [selective fading]?

[4]Is the main focus of the image a technical item, a landscape or people?

[5]How intricate is the content detail?

[6]The three colours fade at different rates.

[7]All three colours fade at similar rates.

Table 5.2: Non-selective fading profile of AF541. The values show the stretch of brightness levels of the image histogram for the overall channel (RGB) as well as the individual colour channels (Red, Green, Blue). This profile was identified as a non-selective profile as all three individual channels varied by similar extents.

Adjustment Channel	2	3	4	5	6
RGB	0-238	0-238	0-238	0-238	0-238
Red	52-255	89-255	136-255	146-255	150-255
Green	28-244	23-244	18-244	13-244	10-244
Blue	0-230	0-220	0-210	0-200	0-190

Table 5.3: Selective fading profile of AF419. The values show the stretch of brightness levels of the image histogram for the overall channel (RGB) as well as the individual colour channels (Red, Green, Blue). This profile was identified as a selective profile as while the red channel stretch varied over time, the green and blue did not.

Adjustment Channel	2	3	4	5	6	7
RGB	0-255	0-255	0-255	0-255	0-255	0-255
Red	23-255	48-255	77-255	110-255	130-255	150-255
Green	0-255	0-255	0-255	0-255	0-255	0-255
Blue	0-255	0-255	0-255	0-255	0-255	0-255

of degraded image stages) in each set were randomly determined to limit any bias dependent on the number of stages of degradation.

The photographs were printed straight as chromogenic-type prints on Fujicolor paper with a gloss finish. Once the images were digitally degraded and printed, the original image was labelled 1. The others were given a random number determined using a random number generator[8]. Each set of photographs of the same image was then placed in a transparent plastic bag and presented to workshop participants in this manner. Hence, in total there were 15 sets with each set containing between 5-7 pieces showing the same image digitally degraded to varying extents. The participants removed the photographs from the plastic bags for assessment.

5.2.1.2 Assessor Questionnaire

A questionnaire was devised to gauge responses from participants (Appendix C). The categories used for classification of images was as described in BS ISO 20462-

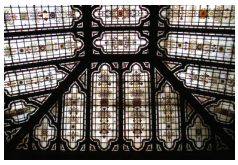
[8]Random numbers in this project were generated using the random number generator built by Mads Haar found at http://www.random.org/

(a) Photo 1.

(b) Photo 2.

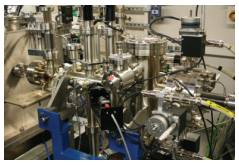
(c) Photo 3.

(d) Photo 4.



(e) Photo 5.

(f) Photo 6.



(g) Photo 7.

(h) Photo 8.

(i) Photo 9.

(j) Photo 10.

(k) Photo 11.

(l) Photo 12.

(m) Photo 13.

(n) Photo 14.

(o) Photo 15.

Figure 5.1: Images of photos used in assessment workshops.

Table 5.4: Photos assessed during the workshops and their characteristics.

Photo	Content	Pieces	Saturation	Fading profile	Memory colours	Details	Age (yrs)
1	Landscape	6	Yes	Non-selective	No	High	0
2	Technical	5	No	Selective	No	Low	32
3	People	7	Yes	Non-selective	No	Medium	0
4	Technical	5	No	Selective	Yes	Medium	0
5	Technical	6	No	Non-selective	Yes	High	0
6	Technical	6	Yes	Non-selective	No	Low	0
7	Technical	7	No	Selective	Yes	High	0
8	Landscape	7	Yes	Selective	No	Medium	0
9	People	5	Yes	Selective	No	Medium	0
10	People	6	Yes	Non-selective	No	Medium	0
11	People	5	No	Selective	No	Low	0
12	Landscape	6	No	Non-selective	Yes	Medium	0
13	Landscape	5	Yes	Selective	No	Medium	0
14	People	6	No	Non-selective	Yes	Low	20
15	Landscape	6	No	Non-selective	No	Low	16

2:2005 [184]. Assessor characteristics, such as knowledge of the material, ratings of interest in different aspects of photographs (aesthetic, material, information) and job were also gathered during the workshops via self-assessment.

5.2.1.3 Workshop Participants

Assessors from five stakeholder categories were targeted - conservators, scientists, collection managers/archivists, curators/custodians and archival users[9]. The invitation to the workshops was circulated either by directed e-mails to interested parties or by posting on relevant mailing lists and blogs, including photoconservation, British Photographic History, National Records of Archives, the AHRC/EPSRC Science and Heritage programme website and the UCL Centre for Sustainable Heritage Mailing list. Participants could then sign up using an online event registration website. In total, 85 participants signed up and attended. This was considered satisfactory as it represents the sample size needed for a significant Pearson product-moment correlation with a medium effect size and a power[10] of 0.80.

[9]This group was composed of participants who identified most closely with using the objects in archives for research purposes.

[10]Power refers to the probability of falsely accepting the null hypothesis. This is usually set at 0.80.

5.2.1.4 Fitness-for-Purpose Assessment Workshops

The majority of the workshops were carried out in a well-lit room in the UCL Centre for Sustainable Heritage, Heritage Science Laboratory (CSH-HSL). The rest of the workshops were carried out in a well-lit conference room at TNA.

The workshops started with a presentation about fitness-for-purpose and the informational value of photographs in archives. Instructions for the assessment exercise were then given as follows:

> "On the screen (Figure 5.2) there is the question which we will be assessing during this assessment exercise, and the categories as defined in the British Standard on image quality.
>
> On the left-hand side of the sheet given there are the set numbers which correspond to the number on the bags containing the sets of colour photographs. In each bag, one of the photographs is labelled 1, which is the original. The other numbered photographs have been degraded to different extents in different manners. We will classify the photographs in terms of information content using the 1-5 categorisation scale. If you consider photograph labelled 4 to be unacceptable in comparison to the original (1), then write 4 in the unacceptable column in the respective row. As you might realise, categories have not been preassigned with a meaning, as the aim of this exercise is to try and find out what the categories mean to you. We would like to ask you to use this rating scale for the experiment and we will discuss how you interpreted and used the rating scale at the end.
>
> If you have any questions, please let me know."

During the assessment assessors worked individually. Each participant took one set at a time at random until they had rated all sets. Following this, the second sheet of the assessor questionnaire was distributed and a discussion was held on the workshop and the project. The third questionnaire sheet was circulated at the end of the workshop. The distribution of questionnaire sheets was staggered to ensure that questions on subsequent sheets did not influence those on the previous one.

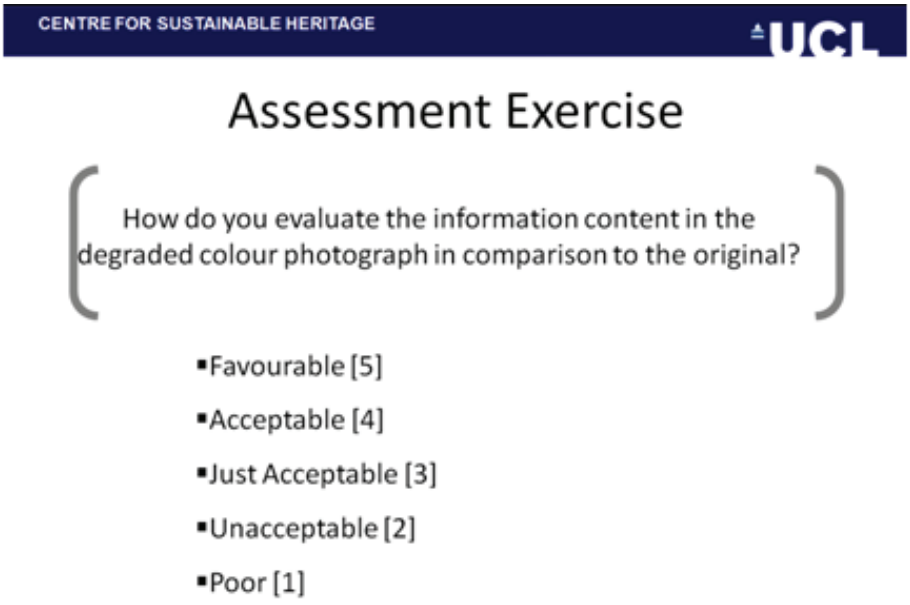


Figure 5.2: Question and classification as used with the fitness-for-purpose assessment workshop participants.

5.2.1.5 Data Analysis

ΔE_{RGB} was calculated based on the degradation profiles used. For each photograph in a set, the corresponding ΔE_{RGB} was calculated and plotted against the classification given for that photo by each participant. The value for ΔE_{RGB} corresponding to a categorisation of 2 (unacceptable) was calculated (Figure 5.3). This value was defined as the 'unacceptability threshold'.

Cases where participants rated no change in rating for all photographs and also where errors were introduced, when the plot of photo classification against photo ΔE_{RGB} had an $R^2 < 0.6$, were discarded. This ensured that only cases where there was at least a moderate correlation between ΔE_{RGB} and categorisation were used. As this resulted in less than 5% missing data, the remaining data set was considered to be satisfactory and still highly representative. The resulting missing data was replaced by the mean for that photo.

Statistical analysis of data was carried out using IBM SPSS Statistics 19 software package. A significance level of $p < 0.05$ was used for all statistical tests[11].

[11]Non-parametric analogues of these tests were also investigated. The same pattern of results was obtained using these tests.

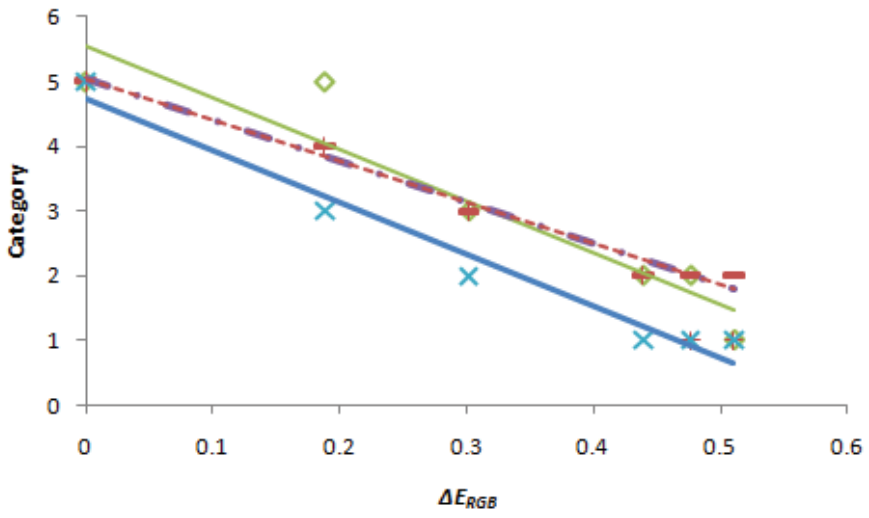


Figure 5.3: Typical plot of classification classes vs ΔE_{RGB} for four participants for the same photograph. A category of 2 corresponds to an unacceptable rating.

One-Way ANOVA The one-way between groups ANOVA test compares the mean of three or more independent data sets and confirms if the means of these sets are statistically significantly different or not [194]. The hypotheses tested were:

H_0: The data sets have means that are not statistically different.

H_1: Some of the means of the data sets are not equal.

The null hypothesis was rejected if the p-value was less than 0.05.

Pearson's Correlation Coefficient The Pearson's correlation coefficient is used to measure the association between two continuous variables, such as ratings of experience and knowledge. A correlation close to +1 indicates a very strong positive correlation, while a correlation close to -1 indicates a very strong negative correlation. A correlation coefficient close to 0 indicates no relationship between the two variables [194]. The hypotheses tested were:

H_0: There is no correlation between the two variables.

H_1: There is a significant correlation between the two variables.

The null hypothesis was rejected if the p-value was less than 0.05.

Repeated Measures ANOVA The one-way repeated measures ANOVA test is used when the same participants take part in three or more cases in an experiment

(e.g. the same participant rated each photograph). As for the one-way between groups ANOVA test, it compares the mean of a number of data sets and confirms if the means of these sets are statistically significantly different or not [194]. The hypotheses tested were:

H_0: The data sets have means that are not statistically different.

H_1: Some of the means of the data sets are not equal.

The null hypothesis was rejected if the p-value was less than 0.05.

Principal Component Analysis Principal Component Analysis (PCA) seeks those linear combinations of the variables investigated that account for the greatest amount of variation in the set of variables. PCA is, therefore, used to reduce the number of variables. In this work, it was used to provide a qualitative description of the relationship between different variables. In this case, the variables shown in Table 5.4 were used.

5.2.2 Results & Discussion

As has been discussed in the introduction to this section, the objective of this study was to determine the magnitude of colour change considered unacceptable with respect to the fitness of an archival chromogenic print to convey information. However, two aspects that could affect the outcome had to be investigated first. These were the effect of the participants attending the workshops, as well as of the selected prints on the outcome.

5.2.2.1 Influence of Assessor on Unacceptability Threshold

It was of interest to understand if the assessor characteristics as determined through the questionnaire had an effect on the obtained Unacceptability Threshold (UT). This was of concern as, should discrepancies be present, an estimation of the UT could be biased.

For this reason, a number of assessor characteristics were determined prior to the workshops. These related to the various modes of engagement an assessor might have when interacting with colour photographs and archival materials. Assessors were, therefore, identified in five stakeholder categories as discussed above (p. 118) to represent these different modes of engagement.

The average and median UT for the different stakeholder groups is shown in Table 5.5. This shows that the UT for the different assessor categories varied from 0.44 for scientists to 0.49 for curators and custodians. The median was slightly lower in each case and varied from 0.41 for scientists and 0.47 for collection managers and archivists. However, a one-way ANOVA showed that there was a non-significant effect of the assessor group on the UT, $F(4, 80) = 0.21\text{-}1.14$, $p > 0.05$.

Table 5.5: Descriptives by assessor participant category.

		UT (ΔE_{RGB})		
	N	Median	Mean	Std Deviation
Conservator	43	.42	.45	.17
Scientist	13	.41	.44	.15
Collection Manager/Archivist	9	.47	.48	.16
Curator/Custodian	7	.45	.49	.17
Archival User	13	.44	.46	.16
Total	85			

During the workshops, participants were also asked to respond to a number of questions dealing with their experience and knowledge of photographs. Correlation analysis was carried out to determine if there was any correlation between the UT and assessor characteristics. If correlations were present, the UT could be biased.

Some significant correlations were obtained (Table 5.6). However, there is only limited evidence for a small minority of photographs that assessor characteristics and UT are correlated as most of the correlations are not significant. Hence, it was concluded that there is no clear evidence indicating the influence of assessor background and interest on the UT.

The location in which the workshops were carried out (CSH-HSL or TNA) also showed no difference in the outcome if investigated using a one-way ANOVA, $F(1, 83) = 0.001\text{-}1.049$, $p > 0.05$.

The results obtained in this study corroborate the findings of similar studies [180]. Although it is sometimes expected that 'experts' and 'lay persons' respond differently, the outcome is often similar. The only difference seems to be that experts tend to be more prone to be less forgiving of changes, possibly as they are more trained in detecting changes [180]. As there was no correlation between assessor characteristics and UT, it was, therefore, acceptable to consider all participants as one group for further investigations rather than as subsets of a larger population.

Table 5.6: Table of Pearson's Correlations between Unacceptability Threshold and Ratings of Interest and Experience for each photograph. *0.05> p > 0.01, **0.01> p > 0.001.

	Rating of interest in			Knowledge of	Regularity of dealing with	
Photo	Materials	Information	Aesthetics	colour photography	Prints	Archival materials
1	-.14	.08	-.06	-.20	-.15	.03
2	-.12	.16	.01	-.14	.01	.12
3	-.12	.25*	.01	-.09	-.09	.06
4	-.28**	.16	.06	-.12	-.15	-.13
5	-.04	.03	.02	-.18	-.13	.03
6	-.03	.05	-.01	-.28**	-.31**	-.01
7	-.29**	.05	-.04	-.13	-.16	-.03
8	-.03	.13	.09	-.13	-.23*	-.11
9	-.28**	.10	.03	-.19	-.16	-.05
10	-.10	.10	-.01	-.15	-.14	.02
11	-.11	.08	-.09	.02	.02	.01
12	-.01	.07	-.01	.01	-.10	.10
13	.01	.08	.05	.04	-.06	-.02
14	-.07	.08	-.08	-.06	-.12	-.03
15	-.14	.11	-.07	-.07	-.01	.11

5.2.2.2 Influence of Image Characteristics on Unacceptability Threshold

As discussed (p. 115), photographs showing different content types and a variety of characteristics relating to the intricacy of detail, colour saturation and presence/absence of memory colours[12] were also considered.

The first question considered was whether the UT depended upon the photograph. When analysing the descriptives by photograph (Table 5.7), the lowest UT was 0.31 for photo 2 and the highest was 0.57 for photo 10 (Figure 5.1). The lowest median was 0.29 for photo 2, and the highest was 0.49 for photo 3.

Unlike the influence of assessors on the UT, it quickly became clear that there was a possible association between the UT and the photograph being assessed (Figure 5.4). It was, therefore, essential to investigate this further for the source of these interactions to be identified. This was relevant as, should these differences be based on image variances that could easily be identified for a photograph in a collection, it could provide a way for differentiated management for collections, should this be appropriate.

[12]Memory colours are colours of objects that an observer might reasonably expect to know the colour of e.g. flesh or tree [195].

Table 5.7: Mean Unacceptability Threshold for each photograph.

	UT (ΔE_{RGB})		
	Median	Mean	Std. Deviation
Photo 1	.47	.52	.13
Photo 2	.29	.31	.11
Photo 3	.49	.51	.12
Photo 4	.43	.44	.16
Photo 5	.43	.47	.16
Photo 6	.47	.53	.18
Photo 7	.46	.54	.20
Photo 8	.39	.42	.11
Photo 9	.34	.40	.14
Photo 10	.48	.57	.18
Photo 11	.28	.32	.12
Photo 12	.46	.50	.17
Photo 13	.34	.37	.13
Photo 14	.47	.52	.17
Photo 15	.44	.45	.13

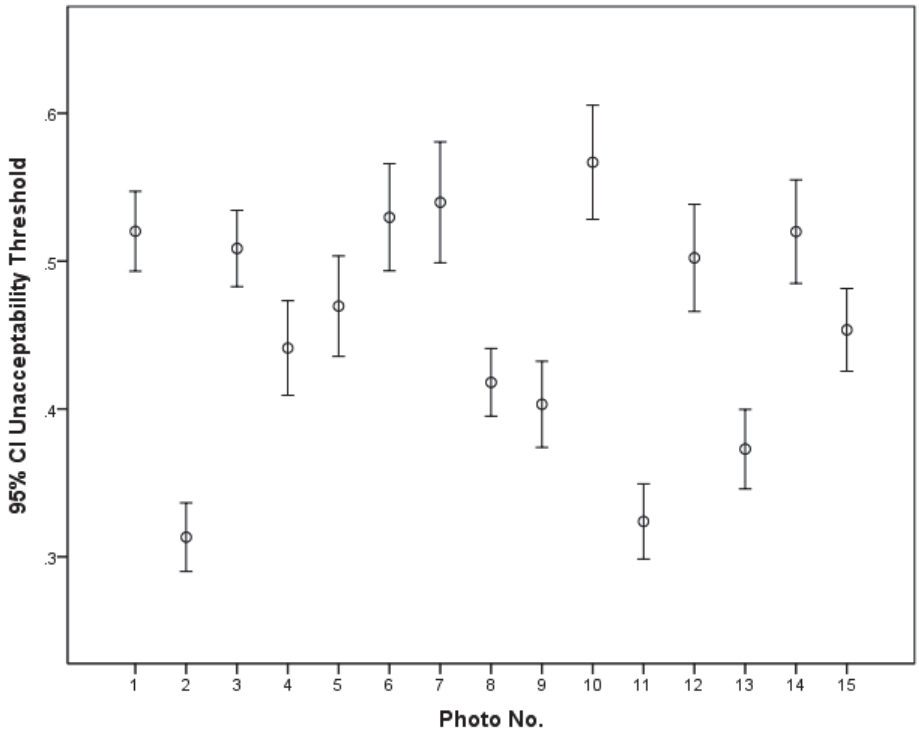


Figure 5.4: 95% confidence intervals for the mean Unacceptability Threshold by photograph.

A repeated-measures analysis was carried out to determine the signficance of variance between unacceptability threshold for various photographs. Mauchly's test indicated that the assumption of sphericity[13] had been violated, χ^2 (104) = 301.26, $p < 0.05$. Therefore, multivariate tests are reported ($\varepsilon = 0.67$) [194]. The results show that the UT was significantly affected by the photo investigated, $V = 0.92$, $F(14, 58) = 56.714$, $p < 0.05$.

The content of an image is possibly a variable that would affect the UT as it might affect the way an assessor interacts with the image. Furthermore, observers are typically more sensitive to changes in colours of an item they are familiar with - 'memory colours' - such as trees [7, 29, 65]. Hence, it was expected that the UT would be lower for images of persons rather than images showing technical details and other inanimate objects.

However, a repeated measures analysis showed that there was no significant effect of Content Type on the UT, $F(2,160) = 1.5$, $p > 0.05$[14]. This could be explained by a comment that regularly arose during workshop discussions. While some assessors said that they found changes in memory colours to be important as they could judge changes in them easily, a considerable number also said that changes in memory colours were not that significant as they knew the colour expected there and, hence, the information was not equally necessary.

Besides content type, the fading profile was also investigated. Two fading profiles - non-selective and selective fading - were investigated in this study as this is known to affect perception; human perception tends to be more affected by selective fading[15], such that less selective fading is often preferable to selective fading of a limited number of the dyes [7, 65].

This was, in fact, the outcome of this study. The results show that the UT was significantly affected by the fading profile $V = 0.92$, $F(14, 58) = 48.48$, $p < 0.05$. It was also an issue commented on a number of times during the discussions. Unfortunately, however, it is difficult to predict the fading profile of a chromogenic

[13]Sphericity is a mathematical assumption in repeated measures ANOVA. It relates to the equality of the variances of the differences between levels of the repeated measures factor.

[14]Mauchly's test indicated that the assumption of sphericity had not been violated, χ^2 (2) = 1.2, $p > 0.05$.

[15]Humans are known to be most sensitive to magenta dye loss and least sensitive to yellow dye loss. Thus, a yellow stain tends to be less objectionable than a stain of another colour [7, 65, 180]. Nevertheless, for many years, cyan was the dye that exhibited the greatest instability [21, 67]. Hence, the selective fading in this case was based on the cyan dye (red colour coordinate in the RGB system).

print due to various possible combinations of dyes.

Another factor that was investigated was if a correlation was present between image age and UT. As presented in Table 5.4, while most of the images had an age of 0, one image in each content class was older, and hence, what was considered to be the original image, labelled 1, was already degraded. This is so as while most of the images were obtained as digital copies of recently obtained photos, the aged images were obtained from developed prints within the research collection. However, a Pearson's Correlation analysis did not show a correlation between age of photograph and UT (r = -0.322, p >0.05.).

To better understand the effect of different factors on the unacceptability threshold, PCA was also carried out. Based on previous studies [7, 65, 180] and the factors previously discussed, the relationship between a number of factors and the UT was considered.

The factors used for PCA are shown in Table 5.4. In particular, the presence/absence of memory colours, the fading profile used and content type were investigated. Also, the extent of intricate details present was investigated, as it was assumed that the more intricate a photo the more likely that information is lost when colours change in the image.

The final aspect was colour saturation[16]. Colour saturation was also included as previous studies seem to have given differing conclusions. While a study by Kartuzhanski and Shubina [180] came to the conclusion that participants were more sensitive to minor colour shifts in pure saturated hues than for white-diluted ones, other studies have determined that observers are more sensitive to changes of neutrally-coloured objects than of brightly coloured objects or of high-contrast scenes with saturated colours and large, dark areas [7, 29, 65].

The results obtained by PCA are shown in Figure 5.5. The PCA only explains 53% of variance and, hence, any conclusions have to be treated with caution. Nevertheless, the results do confirm that content type does not seem to be associated with the UT. It is of interest that technical content did not group with the other two content types.

From this investigation, it can be observed that the factors most closely correlated with the UT were the fading profile and the extent of intricate details present in the image. There are several possible explanations for this result. A possible

[16]Colour saturation refers to the dominance of hue in the colour

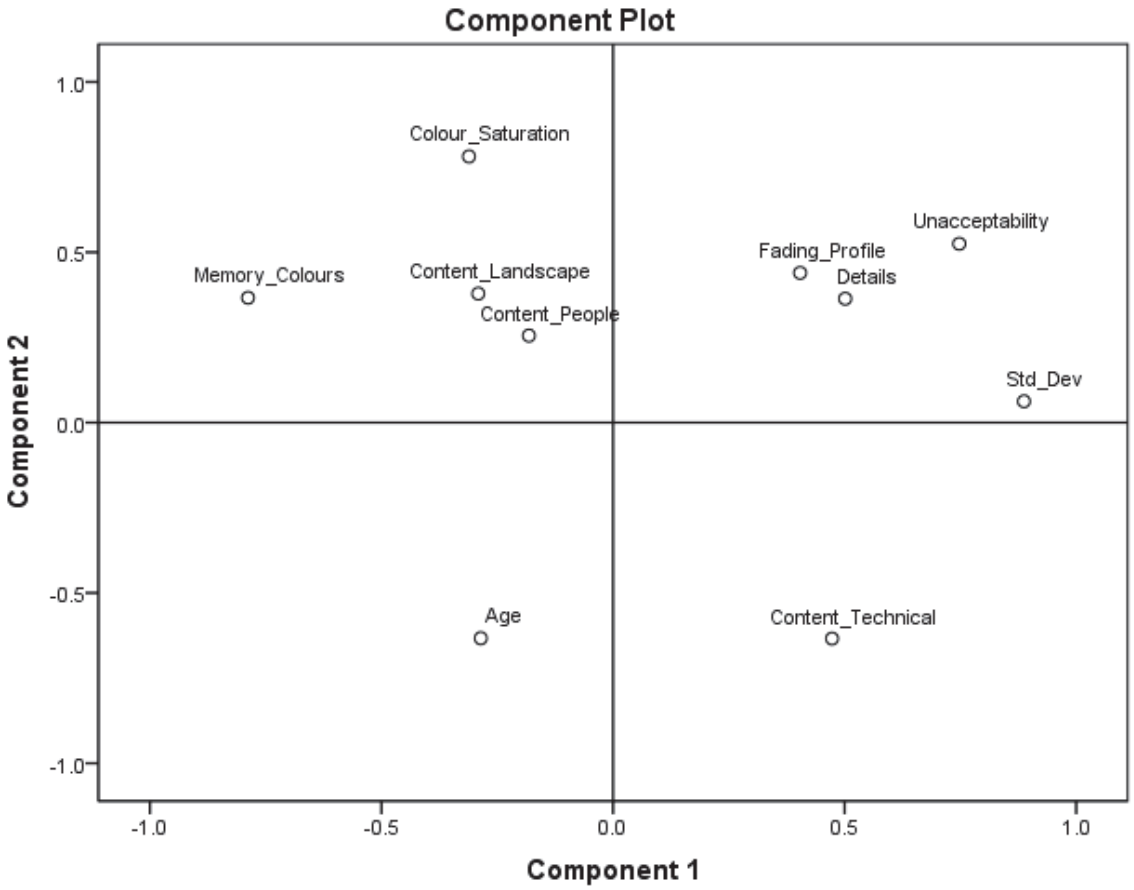


Figure 5.5: Principal Component Analysis loading plot. Component 1 represents 29% of the variance. Component 2 represents 24% of the variance (total 53%).

explanation for the effect of fading profiles could be that selective fading causes changes in contrast much more quickly than non-selective fading. Hence, information present in tiny intricate details is more easily lost, causing an earlier point of unacceptability.

Furthermore, the more intricate details present in a photo the more information that is likely to be lost and, hence, the earlier is the determination of unacceptability. In the case of these workshops, it is also likely that when an image possessed a greater degree of intricate details, it was more likely that a workshop participant had picked on some of these details to qualify their decisions on and, hence, result in an earlier unacceptability outcome.

It is possible that the extent of intricate details in an image correlates to the

amount of archival descriptors provided for an object in a catalogue. However, further research is required to establish how complete and uniform such descriptions are within an archival catalogue and if such an extension of the argument could be made before this aspect of image content could be exploited for more directed collection management. This could be a relevant issue for future research, but it was beyond the scope of this project.

5.3 Conclusion

The processes by which an object is associated with value to the society and then loses value through damage and loss are complex and dynamic [196]. Although these processes are often considered central to heritage studies, methodologies for assessing them are not well established.

The value considered to be of greatest relevance to archival materials is the informational value. Hence, it is the fitness of chromogenic prints to carry information that had to be assessed. Most value assessment methodologies applied to heritage studies to date fall into two broad categories: anthropological/ethnographical and economic valuation methodologies. Though they have been widely implemented in the field, there are some key problems with both these methodologies in relation to the expected outcomes of this project, which is why they have not been used. Psychophysical methodologies, on the other hand, are typically implemented for the assessment of image quality.

The methodology designed for the assessment consisted of a categorisation task for a number of series of sequentially degraded images. The evidence from this study suggests that the assessment of the fitness of a chromogenic print within an archival collection is not affected by assessor characteristics.

However, the same cannot be said for the effect of image content on unacceptability threshold. Regrettably, the factors identified as most significantly affecting the unacceptability threshold, i.e. fading profile and details, are not factors that can be easily determined for an object in a collection as methods yet need to be developed.

Furthermore, the findings in this study do not cover all the possible circumstances and conditions. First of all, it is a well known fact that the conditions of viewing affect the perception of viewers. Fading in a reflection print viewed in a

well-lit location would be more apparent to the observer than the equivalent fading to an image observed in a darkened environment where the eye is already accustomed to the lower colour intensities [65]. Secondly, the study only looked at paired comparisons rather than single stimuli. This approach was chosen to limit the effect of image content on the assessments. However, when an original reference point is available for an image, the extent of fading tends to be more obvious than for an image viewed in isolation from other stimuli [7, 65].

Nevertheless, these results indicate that the overall UT is the best estimate of the ΔE_{RGB} considered as unacceptable for objects in archival collections and, hence, defining the end of their lifetime. A cumulative frequency representation of UT is shown in Figure 5.6. As the median (0.43) provided an estimate of unacceptability faster than the average (0.46 ± 0.16), the median was considered for the rest of this study.

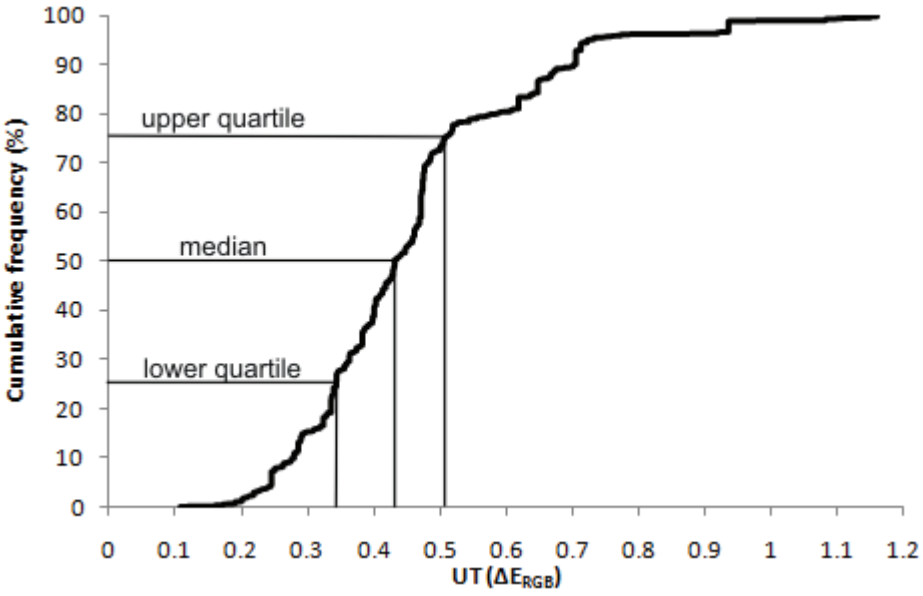


Figure 5.6: A cumulative frequency graph in % for the UTs extracted from the assessment workshops. The median, upper and lower quartiles are marked.

For these reasons, the outcomes of this study might suggest an unacceptable change faster than other circumstances would dictate due to the good lighting conditions and the paired comparison methodology used, as well as the fact that the median was used. However, when dealing with sustainability and managing change, as is often the case in heritage institutions, it is often advisable to err on the side of

caution.

This part of the project was designed to determine the extent of change that is considered to be unacceptable for a colour photograph in an archival context. These two aspects - material and value - will be integrated with environmental aspects of the research into a single model in the chapters to follow.

Chapter 6

Integration of Research Lines

Having looked at the environmental, material and values lines of research individually, it is now appropriate to integrate them. In particular, having identified the critical environmental parameters, it is necessary to determine the extent of their effect on material degradation and value loss.

6.1 Image Degradation

From the work presented so far it is clear that the image, composed of dye chemicals, is the most unstable aspect of chromogenic prints. The image is also most often the reason for a photograph to enter an archival collection. This makes it essential to understand the way images degrade under different environmental conditions of storage.

Dye degradation in colour photographs typically occurs via one of two primary pathways: photodegradation and dark (or thermal) degradation, the latter being either a consequence of instability induced during processing or long-term dye instability [65, 197, 198]. Archives typically do not have much control of processing methodologies. Therefore, as established by Reilly [3], "from an archival perspective, the best way to guarantee long life for a colour photograph is through storage, not through product selection".

Photodegradation tends to cause a disproportionate amount of dye density loss in lower dye density areas and highlights [7, 17]. Magenta dyes are typically the most susceptible to photodegradation, resulting in cyan or greenish coloured prints when prints are left on display [21]. However, since archival storage implies dark

storage, it is expected that light induced degradation contributes minimally to the overall degradation.

'Dark fading', a term often used in technical literature, refers to chemical degradation in the absence of light, promoted mainly by heat, but also by other factors, particularly humidity and other atmospheric conditions [17, 198]. This slow, but ever-present, image deterioration, starts from the moment the image is developed. The typical consequences are overall colour shifts and a yellowish stain [7]. Until the 1980s, cyan dyes were generally more susceptible to dark fading, resulting in reddish images when the prints are stored in dark conditions [21]. In the absence of light, this is the pathway of greatest concern for chromogenic prints stored in archival collections.

Significant improvements have been made in the chemistry of the image over time. This rendered younger chromogenic prints more environmentally stable in comparison to the older chromogenic prints. Nevertheless, environmental conditions remain the principal cause of chromogenic print fading [17, 197]. In fact, Tuite [65] states that "no [silver-based] colour photographic product yet has archival stability under all conditions of use, particularly the early products".

This is still generally true, although the stability has increased around four-fold in the last forty years or so, mainly due to advances in coupler chemistry [199], as print stability is just one of numerous factors that photographic companies aspire for. Hence, stability is competing with other pressures that might be antagonistic when new and improved products emerge on the market. Therefore, determining how these prints would behave under various environmental conditions is of interest.

The true measure of the adequacy of colour image stability is how the images endure the storage conditions [65]. However, since chemical reactions involved in the degradation processes are too complex and too slow, studying the natural degradation process at its own pace is often not feasible. Thus, accelerated degradation is often used.

6.1.1 Accelerated Degradation

Accelerated degradation is thought to indicate "in a relatively short period of time what will happen to materials [...] over a period of years" [200]. This type of research, particularly when used in relation to prediction, has often been criticised.

However, in the last years, significant progress has been made in realising its potential, as well as recognising its pitfalls [76].

Accelerated degradation involves speeding up rates of degradation reactions [7] and is typically used in heritage science:

- To establish in a short time the comparative chemical stability or physical durability of materials or material ensembles.
- To predict the lifetime of materials under expected conditions of use.
- To help elicit information about the mechanisms of degradation and their effect.
- To determine whether a certain intervention would prolong the lifetime of an object or its material [76].

Accelerated degradation experiments may rapidly provide information necessary in product development. In addition, as is the case of this thesis, they also provide information necessary for long-term prediction of stability under storage conditions [65].

Chemical reactions are, with rare exceptions, accelerated at higher temperatures. The rule of thumb for reactions involving water is that for each 10 ℃ rise in temperature the rate of reaction approximately doubles [29]. However, more accurate calculations are possible using the Arrhenius equation:

$$k = Ae^{\frac{-E_A}{RT}}$$

where k is the reaction rate constant; A is the pre-exponential factor; E_A is the activation energy; R is the gas constant; and T is the temperature (in K). In fact, a study of values calculated from the Arrhenius equation indicated that for average organic materials, the approximation is 5 ℃ [190]. For an average organic material, E_A would thus be 100 kJ/mol.

However, although heat is often an important rate-controlling parameter in degradation processes, it is generally not the only one. Water (RH), oxygen and other gases also importantly affect stability [76]. Some sources state that RH is the most important factor in the degradation of photographic images [1]. This is possibly the case with materials swelling under the influence of moisture, such as gelatine.

Chromogenic dyes may also be strongly affected by moisture, although they are generally more resistant if in a hydrophobic coupler solvent (typical of the Kodacolor principle), than if in a hydrophilic environment (typical of the Agfacolor principle) [58]. It is, however, worth remembering that the Kodacolor principle is now the main coupler system used [1].

Therefore, besides increasing the temperature, there are other possibilities for acceleration of chemical degradation processes, depending on the factors being investigated. In experiments involving dark fading heat and humidity, but also pollutants, are typically used to influence the rates of chemical reactions involved in image degradation [65, 201].

This Chapter explores a number of different environmental parameters and assesses their effect on dye degradation. First, the effect of pollutants on chromogenic prints is investigated with the aim of identifying the pollutant of greatest interest. Development of a multiparametric dose-response function taking into account the effect of temperature (T), RH and concentration of the prioritised pollutant is then possible. Finally, the use of hypoxic environments on chromogenic print stability as a method for enhancing the lifetime of these prints is examined. The aim of this Chapter is to explore the possibilities to predict the lifetime of chromogenic prints under the expected conditions of storage in mixed archival collections. This methodology is developed further in Chapter 7, where predictive tools are developed.

6.2 Effect of Pollutants on Chromogenic Prints

In Chapter 3, the promoting effect of pollutants on degradation of chromogenic prints is discussed alongside heat and humidity. However, it is difficult to discuss pollutants as a single environmental factor, as individually they react with objects differently. Hence, it was relevant to identify the pollutant that is of greatest concern for prioritisation in the rest of the investigations, as in laboratory conditions it would be very difficult, if not practically impossible, to take into account several pollutants simultaneously.

Although chromogenic prints are typically considered to be less sensitive to pollutants than black-and-white silver photographs [29], pollutants, such as ozone, nitrogen dioxide and sulfur dioxide, are known to react with the gelatine binder [17]. A study by Nguyen et al. [202] determined that nitrogen dioxide and sulfur diox-

ide increase the swelling of gelatine films, particularly for unhardened gelatine, in demineralised water, and change the size-exclusion chromatographic profile of the gelatine, indicating hydrolysis of gelatine. Also, atmospheric pollutants are known to cause yellowing of organic materials, such as dyes [58].

So far there has been limited discussion of the effect of pollutants on chromogenic dyes. Sulfur oxides, nitrogen oxides and ozone have been studied [17, 197]. However, in the environmental monitoring campaign discussed in Chapter 3 VOCs, particularly acetic acid, were also identified as pollutants of potential interest due to their high concentration within archival boxes. Therefore, it was necessary to consider the effects of both indoor and outdoor generated pollutants on chromogenic prints.

In this section, the effect of nitrogen dioxide, acetic acid and formaldehyde is investigated. Acetic acid and nitrogen dioxide were selected for further study as acetic acid and the nitrogen oxides were the indoor and outdoor-generated pollutants, respectively, found in greatest concentration in archival boxes[1]. Formaldehyde was investigated as it is known that some pyrazolone couplers are particularly sensitive to aldehyde vapours [67, 203]. Hence, the effect of formaldehyde on image degradation was also investigated.

6.2.1 Methodology

6.2.1.1 Degradation Experiments

25 photographic prints were selected at random for investigation from the research collection discussed in Section 2.3. Samples of 6 mm diameter were taken from uniformly coloured areas of the selected photographic prints and attached onto a stainless steel wire using a cotton thread and placed in 100 mL closed glass vials (Figure 6.1). The vials were placed in a ventilated laboratory oven (Carbolite, Model PF200) at 80 ℃ and flushed with a stream of air humidified at 60% RH (Instruquest, V-Gen Model 1), containing 250 ppb of a pollutant (VICI Metronics, Dynacalibrator Model 150), every second day for two weeks. Three pollutants were investigated: acetic acid (permeation device: VICI Metronics, p/n 120-005-2851-F56-U60), nitrogen dioxide (permeation device: VICI Metronics, p/n 140-693-0081-U30) and formaldehyde (permeation device: VICI Metronics, p/n 100-005-2300-

[1]Nitrogen dioxide was selected as the nitrogen oxide of interest as it is more reactive than nitrogen monoxide

T53-U70). A control was also set up where no pollutant was added. Colorimetric measurements of the samples were performed every time the vials were flushed.

Figure 6.1: The experimental reactor: 6 mm diameter samples of photographs are threaded together using a cotton thread twisted around a stainless steel coil. The cap with two ports allows for the reaction vessel to be flushed with air of a desired composition.

A schematic representation of the set-up is presented in Figure 6.2. This set-up was devised to allow for different combinations of environmental factors, namely T, RH and pollutant concentration to be controlled, and their effect investigated systematically.

6.2.1.2 Colorimetry

Colorimetric reflectance spectra were measured using an X-Rite 530 SpectroDensitometer (D50/2° observation conditions, standard white background).

6.2.1.3 Data Analysis

sRGB (standard RGB colour model) values were calculated from the reflectance spectra (p. 91). The sRGB colour space was found to be most suitable to monitor

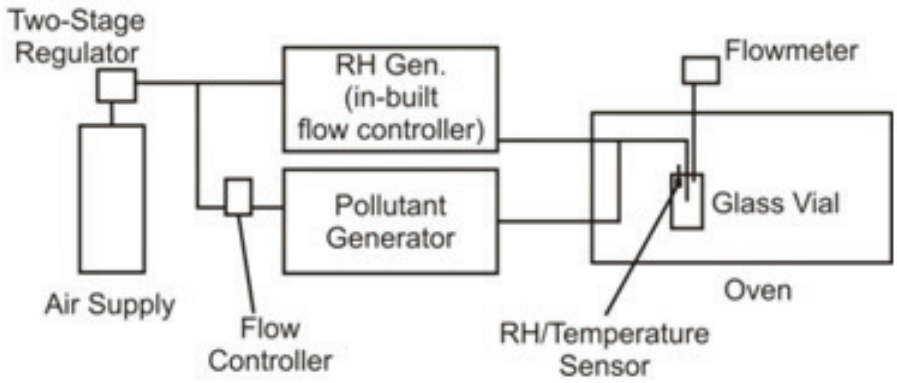


Figure 6.2: Scheme of the experimental setup for accelerated degradation experiments.

changes in dye concentrations due to the complementarity of red, green and blue to the cyan, magenta and yellow dyes, respectively. The measured values after degradation at time t, were normalised against the initial values and the rates of degradation were then determined for each colour coordinate by calculating the slopes of R_t/R_0, G_t/G_0 or B_t/B_0 vs. time.

6.2.2 Results and Discussion

The colorimetric non-destructive method described in Chapter 4 allowed for regular monitoring during accelerated degradation experiments, and thus to monitor relative changes in dye concentration over time. The plot of relative sRGB values over time shows that the degradation reactions are zero-order, as the nature of the plotted graphs is linear (Figure 6.3). This could be due to initial dye concentrations being high enough so that minor changes did not affect the overall concentration of the dye significantly. This observation was found to be valid throughout the useful lifetime of most photographs. This experiment also confirmed that dyes present in chromogenic prints do not necessarily degrade at similar rates; in Figure 6.3 it is evident that the yellow dye (represented by the B coordinate) was the least stable. This is important because, as discussed in Chapter 5, human perception is particularly affected by non-equivalent fading [7, 65].

It is apparent from these results that both positive and negative changes are possible. A positive change in an RGB value indicates a decrease in dye concentration (dye concentration of the CMY dyes are complementary, and thus inversely proportional to the RGB values), as typified by degradation of the dye molecule.

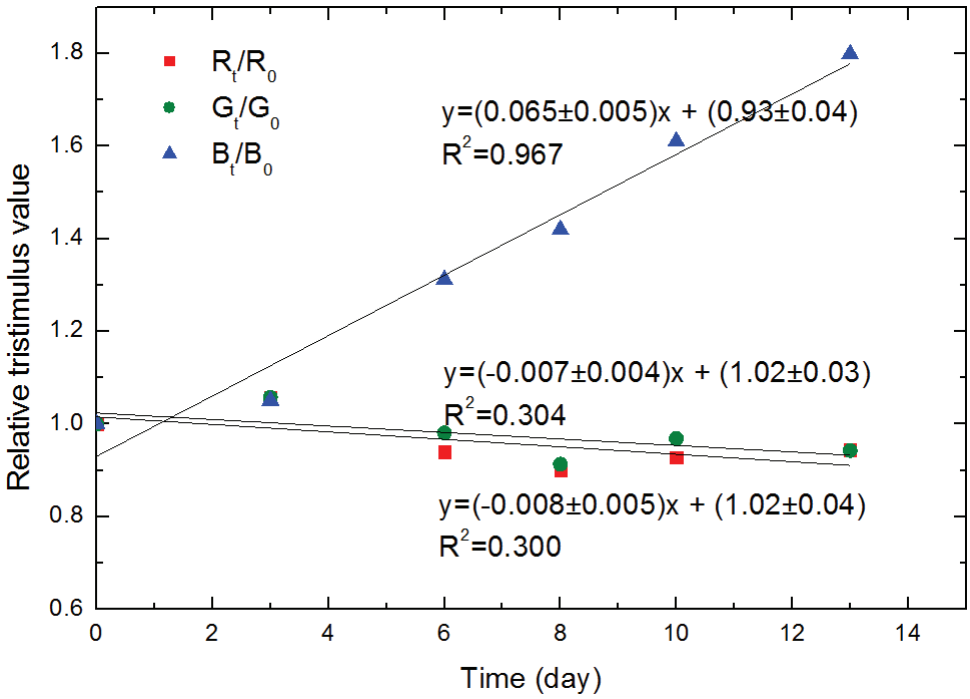


Figure 6.3: Relative changes in sRGB values against time of degradation for a photograph developed in 2005 (Kodak) and degraded in air with 250 ppb acetic acid, at 80 ℃ and 60% RH [204].

However, negative changes in RGB values, indicating an increase in colour intensity, are also possible. This is often the result of either the production of coloured degradation products or, alternatively, of the residual couplers in the photographic paper reacting during the degradation experiment [53, 67, 199].

Having calculated the rate of RGB change for the samples degraded in the presence of different pollutants, a comparison was made of the effect of different pollutants of interest on the rate of dye degradation over time. As evident from Figure 6.4, not all photographs are affected in the same way by all pollutants. This can be explained by the fact that different dyes have been used by different manufacturers at different periods of time. Also, the quality and quantity of the gelatine layer, in which the dyes are embedded, may affect the susceptibility of dyes to degradation in a polluted environment [205].

It is clear that acetic acid causes the most pronounced degree of change when compared to other pollutants of interest at the same concentration. The effect of nitrogen dioxide is less pronounced or similar to that of acetic acid. However, in light

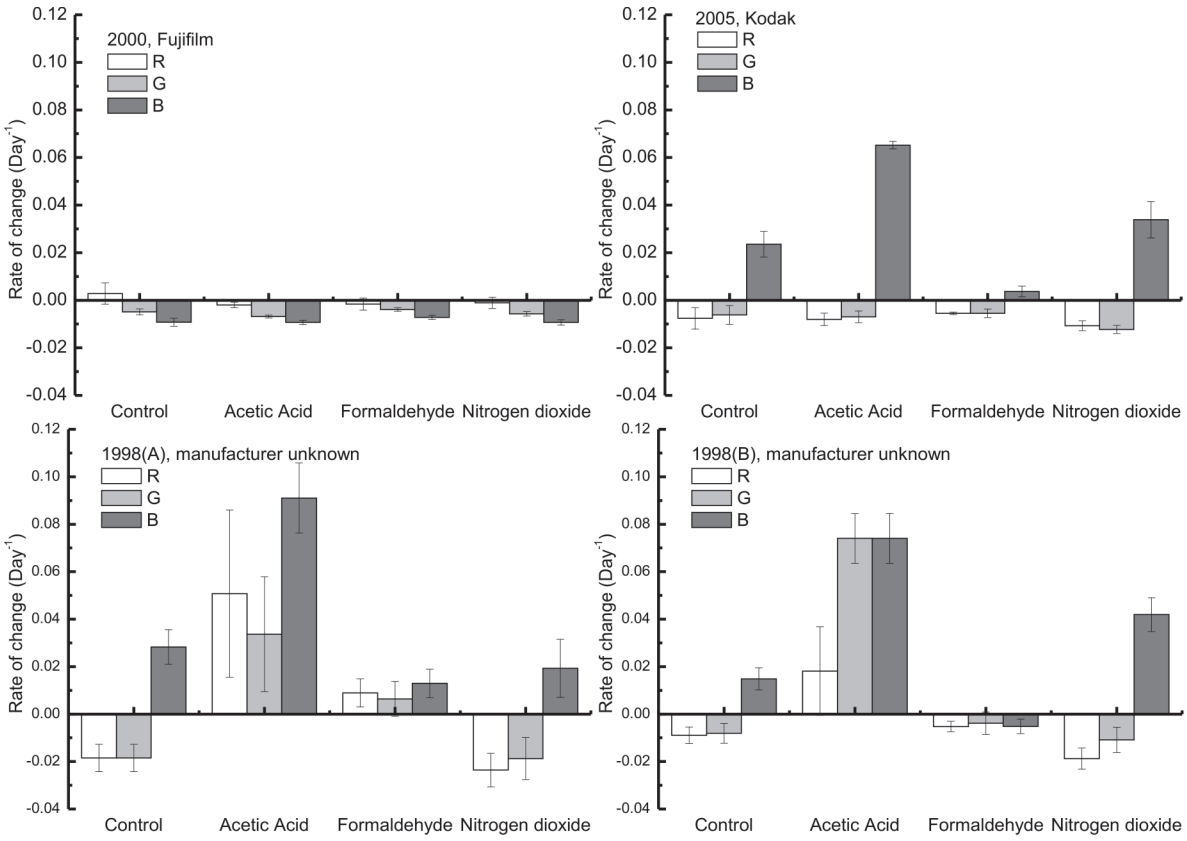


Figure 6.4: Rates of change of dye concentration (expressed as slopes of $\Delta(R_t/R_0)$ vs. time, analogously for G and B), for photographic print samples degraded at 80 ℃, 60% RH, in different environments: air (control) or 250 ppb acetic acid, formaldehyde or nitrogen dioxide, as indicated. The error bars represent uncertainties in the slopes of individual curves, as plotted in Figure 6.3 [204].

of the fact that acetic acid (emitted by archival materials themselves) was measured in archival boxes at concentrations around ten times higher than those of nitrogen oxides (Section 3.3) acetic acid can be identified as the pollutant of greatest concern to chromogenic prints in archival conditions. Nevertheless, in indoor environments where the concentration of outdoor-generated pollutants is more significant (such as in non-filtered environments with high air exchange rates) and with no significant source of indoor-generated pollutants, the effect of nitrogen oxides or other pollutants, particularly ozone, may be prevalent.

Formaldehyde was also determined to be a pollutant of potential concern. While

it is not present in high concentrations in archival environments, it is intensively emitted by paper during degradation [117]. Interestingly, formaldehyde was shown to have a protective effect, i.e. the observed rate of change in the presence of this pollutant was lower than in the control experiment in all four case studies in Figure 6.4. This occurred even though most dyes, particularly yellow and magenta dyes, are known to be susceptible to oxidation, and formaldehyde could contribute in the process as an autoxidation initiator.

Its apparent protective effect is therefore significant, especially since formic acid, if formed by oxidation of formaldehyde, could have a similar effect on the degradation of dyes to that of acetic acid. However, the regular exchange of the atmosphere in the reaction vessel seems to limit the damage, potentially caused by secondary pollutants resulting from formaldehyde oxidation. It is also worth noting that formaldehyde is traditionally used to cure, or 'harden', gelatine [206]. Thus, formaldehyde may be reacting with the gelatine, forming a protective layer around the dyes, preventing their oxidation. Furthermore, aldehyde scavengers, such as *N,N'*-ethyleneurea, 2,3-dihydroxynaphthalene, or Dimedon, have also been introduced by manufacturers to limit degradation by fixing formaldehyde, due to the known degradative effects of formaldehyde on couplers [203]. Hence, while special precautions have been put in place to mitigate the effect of formaldehyde [203, 207–210], few, if any, have been implemented to mitigate the effect of the other pollutants.

Therefore, under conditions of accelerated degradation, acetic acid has a stronger negative effect than nitrogen dioxide or formaldehyde. The latter was even shown to exhibit a slightly protective effect in comparison to the blank experiment. The reason for this could be that due to its known degradative effects on dye components, mitigating factors have been implemented by photographic manufacturers.

The evidence suggests that acetic acid is the most relevant pollutant affecting the lifetime of chromogenic prints in mixed archival collections. This is especially pertinent as acetic acid can be up to ten times more concentrated than any other (indoor- or outdoor-generated) pollutant. Hence, acetic acid was prioritised for further investigations in combination with temperature and humidity.

6.3 Multiparametric Dose-Response Function

All materials eventually decay; chromogenic dyes are particularly sensitive to chemical change. The rate at which this happens depends on the presence of deterioration factors (or agents) in their environment and the effect they have on the objects in question as well as on the composition and condition of the material [132]. As discussed earlier, such data is often obtained through accelerated degradation experiments.

The typical accelerated degradation experiments carried out to predict the lifetime of materials under specific environmental conditions follow the 'one-factor-at-a-time'[2] method of experimentation, as discussed in the previous section. In this method, factors are varied one at a time while the remaining factors are constant. Therefore, this experimental plan provides an estimate of the effect of a single factor at selected and fixed conditions of the other factors.

However, most deterioration agents do not operate independently of each other and changes in one will often influence the effect of another. Therefore, it is also appropriate to investigate the presence of any factor interactions.

An efficient way for planning and conducting such experiments involves principles of Design of Experiments (DOE). DOE has found applicability in a number of research areas. The most common areas involve research for the quantification of the inter-relationship between variables, in the screening of large numbers of variables to identify which are the important factors and in product development to improve products through the reformulation and development of new products [211, 212].

The ideal property of DOE designs is that while several factors are varied simultaneously, each factor may then be evaluated independently. As Box et al. [211] clearly highlight, "if the factors do act additively, the DOE design does the job with much more precision than one-factor-at-a-time methods, and (2), if the factors do not act additively, the [DOE], unlike the 'one-factor-at-a-time' design, can detect and estimate interactions that measure this non-additivity". This gives further strength to the results obtained using DOE [211–213].

Hence, an advantage of DOE is that it allows for the maximum amount of information to be extracted using the minimum number of experiments [212, 213]. DOE is also useful due to its ability to handle experimental error and that it allows for

[2]A factor refers to a deterioration agent, such as T, RH, pollutant etc.

data extrapolation [212].

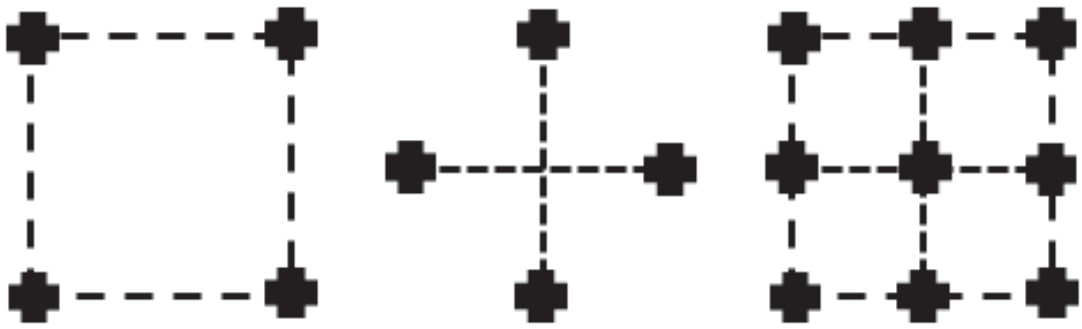
The simplest DOEs are often factorial experiments, where all factors are varied simultaneously at a limited number of factor levels [211]. More complex DOEs involve response surface designs. These methods deal with the understanding of system performance [214, 215].

Central Composite Designs (CCD) are possibly the most popular types of response surface designs. They are very efficient, providing information on the effects of experimental factors and the overall experimental error. CCD may be thought of as a combination of three components (Figure 6.5), namely:

(a) a factorial DOE at two levels,

(b) axial points (star design),

(c) a centre point [157].



(a) Points in the factorial portion of the design are coded to be -1 and +1.

(b) Points in axial (star) portion of the design are at: ($+\alpha$, 0), ($-\alpha$, 0), (0, $+\alpha$), (0, $-\alpha$).

(c) The factorial and axial portions joined to give a CCD. The design centre is at (0, 0).

Figure 6.5: Two-factor face-centred ($\alpha = 1$) central composite design (adapted from [216]).

An option with CCDs is the location of the star-points. Using a face-centred CCD means that the star points are at the centre of each face of the factorial space, so $\alpha = 1$[3]. Thus only 3 levels of each factor are required as opposed to when the star points are located further out of the response surface space. The centre points are

[3]Another typical design is the circumscribed design where the star points are located so that circular, spherical, or hyperspherical symmetry results

also replicated to estimate experimental uncertainty and provide a test for lack of fit [157, 215]. The centre point is generally replicated 3-5 times for spherical CCDs, while fewer may also be possible for face-centred CCDs ($\alpha = 1$) as in this case the star points are not as far from the centre [157, 215, 217].

In this accelerated degradation experimental design, the effect of three factors: T, RH and acetic acid concentration were investigated using a face-centred CCD. Since the degradation of dyes is a chemical reaction, T was expected to have a significant effect on the reaction rate. RH was also investigated as, though the exact effect of water on degradation is not necessarily understood, it is generally known that moisture speeds up the rate of degradation [76, 86].

The third factor investigated was the effect of pollutants. In Chapter 3 it was shown that acetic acid is the most abundant pollutant in archival boxes and in Section 6.2 it was identified as the pollutant most intensively promoting degradation. Hence, acetic acid was selected as the pollutant of greatest interest for this study.

The expected outcome of this study was a multiparametric dose-response function[4] relating the effect of T, RH and acetic acid concentration on chromogenic prints. Such a function can then be used to compare the effect of various environmental scenarios on a collection of such prints.

6.3.1 Methodology

6.3.1.1 Experimental Design

A three-factor, three-level face-centred ($\alpha = 1$) CCD was used to determine the effect of environmental conditions on the rate of colour change. Three independent factors, namely acetic acid concentration (x_1), RH (x_2) and temperature (x_3) were chosen.

Each independent factor had three levels that were -1, 0, and +1 (Table 6.1). A value was then assigned to the -1 and +1 levels for each factor, with 0 being assigned to the middle value. The RH and acetic acid concentration values were chosen to include the typical RH levels present within archival collections. The temperature values were selected as a balance between accelerating the degradation processes

[4] A dose-response function, although in the narrow sense of the term, should be based on the dose actually absorbed, is often used in a wider sense where it is formulated directly in terms of the concentration of an agent in the ambient air, accounting implicitly for the absorption of the degradation agent from the air [218].

such that the effect could be observed within the time limits of the project and not moving too far from the expected storage conditions.

Table 6.1: Uncoded and coded levels of the independent factors. c(AA) refers to acetic acid concentration.

Factor	-1	0	1
c(AA) (ppb), x_1	0	500	1000
RH (%), x_2	20	40	60
T (℃), x_3	50	65	80

A total of 17 different degradation experiments (including three replicates of the centre point) were carried out according to a CCD configuration for three factors (Table 6.2).

Table 6.2: The CCD with three independent factors (coded variables) showing the runs carried out.

Run	x_1	x_2	x_3	Point
1	-1	-1	-1	Factorial
2	1	-1	-1	Factorial
3	-1	1	-1	Factorial
4	1	1	-1	Factorial
5	-1	-1	1	Factorial
6	1	-1	1	Factorial
7	-1	1	1	Factorial
8	1	1	1	Factorial
9	-1	0	0	Axial
10	1	0	0	Axial
11	0	-1	0	Axial
12	0	1	0	Axial
13	0	0	-1	Axial
14	0	0	1	Axial
15	0	0	0	Centre
16	0	0	0	Centre
17	0	0	0	Centre

6.3.1.2 Samples and Apparatus Set-Up

95 photographs were chosen at random from the research collection discussed in Chapter 2.3 to produce a representative collection. The samples cover a range of

manufacturers and dates of production. Sample preparation and apparatus set-up was as discussed in the previous section. Samples were flushed with the appropriate conditions and measured using colorimetry at least three times a week for one month at 80 ℃, once a week for 4 months at 65 ℃ and every two weeks for nine months at 50 ℃ (average of 14 data points per sample).

6.3.1.3 Data Analysis

Colorimetric reflectance spectra were measured at regular intervals using an X-Rite 530 SpectroDensitometer (D50/2°observation conditions, standard white background). sRGB values were calculated as discussed in Chapter 4.

The overall colour change was calculated as ΔE of normalised RGB values:

$$\Delta E_{\mathrm{RGB}} = \sqrt[2]{\left(1 - \frac{R_t}{R_0}\right)^2 + \left(1 - \frac{G_t}{G_0}\right)^2 + \left(1 - \frac{B_t}{B_0}\right)^2}$$

Where ΔE_{RGB} is the total colour change in terms of RGB; R_0, G_0 and B_0 are RGB values prior to accelerated degradation; and R_t, G_t and B_t are RGB values at time t (in days).

The rate of change was calculated as the slope of a graph of ΔE_{RGB} against time (in days). Colour change per year was determined by multiplying the rate by 365. This was defined as the normalised annual colour change of the image, ΔE_{T}:

$$\Delta E_{\mathrm{T}} = \Delta E_{\mathrm{RGB}} \times 365 \text{ days}$$

The ΔE_{T} of the collection of samples used in the experiment was then calculated by averaging the values for all the samples degraded under the environmental conditions of interest.

6.3.1.4 DOE Analysis

Statistical analysis of design of experiment data was carried out using Minitab® 15.1.30.0 (Minitab Inc.) software package.

To fit the model, the rate of degradation, ΔE_{T}, was converted to its natural logarithm, and the temperature was converted to $\frac{1000}{T}$ (in K) to allow for it to follow the Arrhenius equation.

6.3.2 Results and Discussion

The objective of this study was to develop a multiparametric dose-response function that relates the effect of three environmental parameters - T, RH and acetic acid concentration - on the rate of image degradation in chromogenic prints using a DOE approach to accelerated degradation experiments. These were planned following a face-centred central composite design.

To understand the characteristics of the collection, a frequency plot of ΔE_T was examined for all experimental runs. In all cases, the results of a Kolmogorov-Smirnov test showed that normal distribution may be reasonably assumed (Figure 6.6), $Z = 0.836$ - 1.259, $p > 0.05$. This indicated that the photographs can be considered as a single set in the DOE analysis. This would not have been the case had e.g. a bimodal distribution been identified.

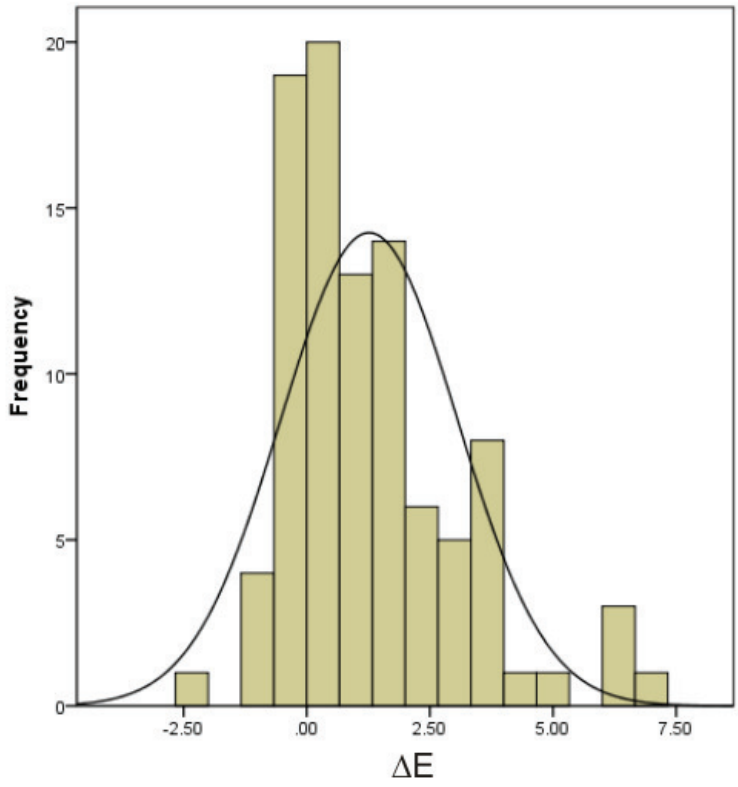


Figure 6.6: Frequency plot of ΔE_{T} for samples exposed to 80 ℃ 20% RH and 0 ppb acetic acid. The samples exhibit a reasonably normal distribution.

As has already been discussed (p. 145), degradation was accelerated by car-

rying out the experiments at higher temperatures than encountered in a typical archival repository. The results obtained had to, therefore, be extrapolated to the temperatures expected in archival collections.

Extrapolations of degradation rates to such temperatures are often obtained using the Arrhenius' equation. Previous investigations within the photographic industry had shown good correlations between Arrhenius test predictions and trade experience and, in fact, this is a widely used methodology in photographic companies, including Kodak [197, 219, 220].

The Arrhenius equation (Section 6.1.1, p. 134) is related to the rate of reaction via the rate constant:

$$rate = k_T[X]^m[Y]^n$$

where k_T is the reaction rate constant at temperature T; $[X]$ and $[Y]$ refer to the concentration of reactants X and Y; and m and n refer to the reaction order for these reactants, respectively. Substituting the Arrhenius equation into this equation gives:

$$rate = Ae^{\frac{-E_A}{RT}}[X]^m[Y]^n$$

Therefore, the rate of reaction and temperature are related as follows:

$$\ln(rate) = \left(\ln A - \frac{E_A}{RT} + m\ln[X] + n\ln[Y]\right)$$

Hence:

$$\ln(rate) \propto \frac{1}{T}$$

Therefore, for this relationship to hold, and for extrapolation to lower temperatures to be possible, natural logarithm of the rate of reaction and inverse temperature should be used in calculations [197]. For this reason, the temperature (in ℃) was converted to *1/T* in 1/K. In addition, the normalised annual colour change, ΔE_T, was converted into its natural logarithm. Due to the significant magnitude difference between the resulting T, RH and acetic acid (AA) coefficients, the temperature parameter was multiplied by 1000.

Having specified the factors, a response surface model could be fitted. As is typical, a linear (first-order) function was investigated first. The regression coefficients for this linear model and results for the linear term are presented in Table 6.3. The

results for uncoded variables are provided, to provide an idea of the relationship between the effects of 1 unit of temperature, RH and acetic acid concentration.

Table 6.3: Regression coefficients for the first order equation and results for the linear term. The regression coefficients are the coefficients used to build the function relating the effect of the factors on the rate of colour change. The t- and p-values are the results for the significance of these linear terms.

Term	Coeff	SE coeff	t-value	p-value
Constant	31.79	0.27	25.04	0.00
c(AA) (ppb)	0.0002	0.00011	1.35	0.20
RH (%)	0.0101	0.0028	3.62	0.00
$1000/T$ (K)	-11.09	0.03	-26.05	0.00
$S = 0.18$; $R^2 = 98.2\%$				

Having developed the DOE function, it was necessary to confirm the adequacy of the fitted function, as an incorrect or under-specified model can lead to misleading conclusions. The statistical analysis indicates that the fitted function was adequate, possessing no significant lack of fit ($p > 0.05$) and with a very satisfactory R^2 (98.2%)[5].

The residuals of the fitted function were also analysed to examine the goodness of model fit. If normal distribution of residuals is to be assumed, the points on the normal probability plot should form a straight line, unless there are less than 50 observations, in which case the plot may display curvature in the tails [216]. The Anderson-Darling statistic determines how well a data set follows a specific distribution (normal in this case). Randomness of residuals is then assessed using the residuals versus fit plot. This plot should show a random pattern of residuals on both sides of 0. Also, there should not be any recognisable patterns in the residual plot.

In this case, both the normal probability plot (Figure 6.7) and the Anderson-Darling statistical analysis ($AD = 0.12$, $p > 0.05$) indicated that the residuals were normally distributed. The residuals versus fit plot (Figure 6.8) shows that the residuals are randomly distributed as no recognisable pattern can be observed. These observations indicated that the function fits the empirical data well.

Once the fitness of the DOE function is confirmed, the coefficients (Table 6.3) can be investigated. It is immediately apparent from the t-value that temperature

[5]The closer the value of R^2 to 100%, the better the empirical function fits the actual data.

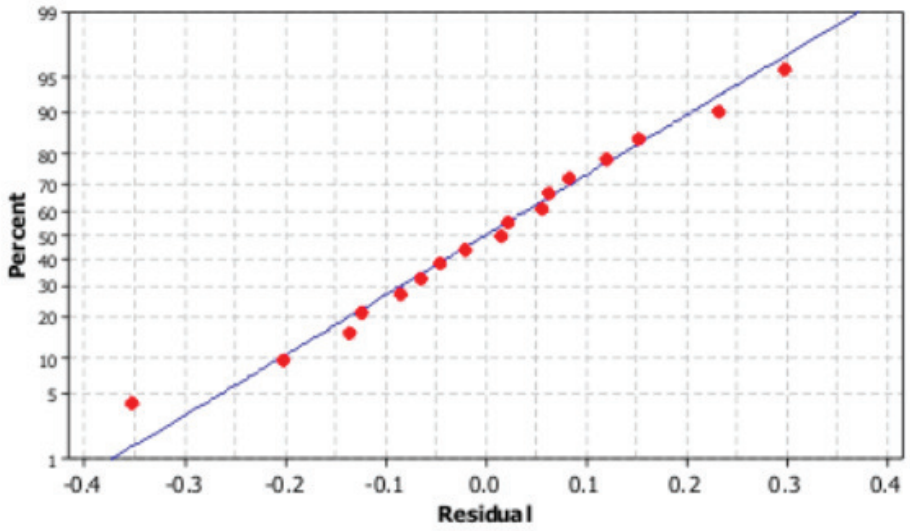


Figure 6.7: Normal probability plot of residuals. The straight line indicates that the residuals are normally distributed, meaning that the DOE function is a good fit. The minor curving at the tails is expected for cases with less than 50 data points, as in this case (n=17).

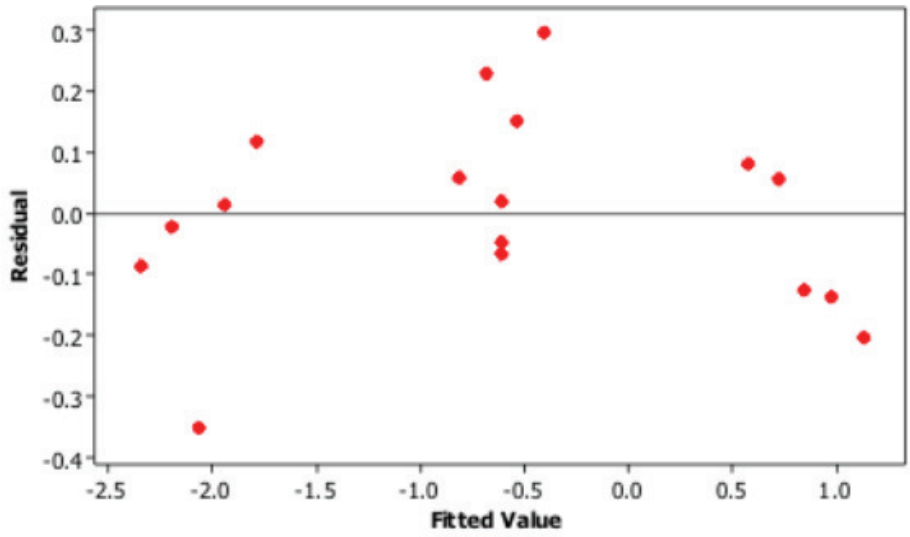


Figure 6.8: Residuals versus fit plot. The random distribution of points on either side of 0 indicates that the residuals are randomly distributed.

has by far the most significant effect on the rate of change. The value of the RH coefficient is around 50 times that of the acetic acid coefficient. The results also indicate that while the effect of RH and T are statistically significant ($p < 0.05$), the effect of acetic acid is not significant based on the data collected ($p > 0.05$).

In relation to the latter, it is important to note that although acetic acid concentration was found not to have a significant effect on the rate of chromogenic prints collectively, this does not mean that it has no effect on individual photos, and that, hence, acetic acid can be allowed to accumulate. The analysis of multiparametric dose-response functions for individual samples, such as the example shown in Table 6.4, confirms this. Statistical analysis indicates that this particular fitted function is also adequate, possessing no significant lack of fit ($p > 0.05$), with a very satisfactory R^2 (99.2%) and normally distributed residuals. The reason for such differences is that individual dyes and, hence, individual photographs, may be much more sensitive to the effects of acetic acid than others, as has been identified already in Figure 6.4.

Table 6.4: Regression coefficients for the first order equation and results for the linear term for one individual sample (1989, Konica)

Term	Coeff	SE coeff	t-value	p-value
Constant	30.83	0.09	-34.84	0.00
c(AA) (ppb)	0.0003	0.0004	3.41	0.01
RH (%)	0.0150	0.0019	7.78	0.00
$10000/T$ (K)	-1.090	0.003	-36.62	0.00
$S = 0.12$; $R^2 = 99.2\%$				

6.3.2.1 Isoperms and Isochrones

An isoperm is defined as a curve describing 'constant permanence' [76]. Feller [76] described them as curves of T and RH connecting points with equal rates of degradation. Isoperms present a very practical tool providing answers to questions such as "If the temperature is allowed to increase by 1 ℃ what is the corresponding decrease in RH that is needed to retain the same permanence?"

Having developed multiparametric dose-response functions comparing the effect of three environmental conditions, two-dimensional isoperms can be calculated by keeping one parameter constant. The isoperm for T and RH is shown in Figure 6.9.

As was used by Sebera [221], a temperature of 20 ℃ and 50% RH were used to represent a permanence of 1. From this isoperm it is clear that a decrease in temperature of 1 ℃ equals an increase of around 13% RH.

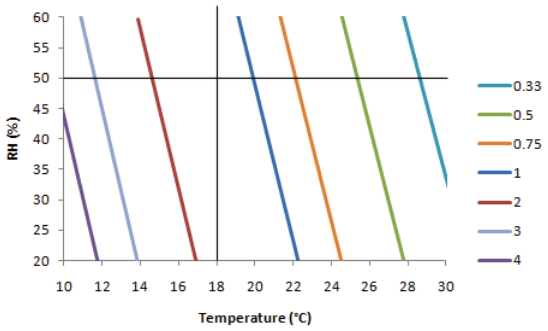


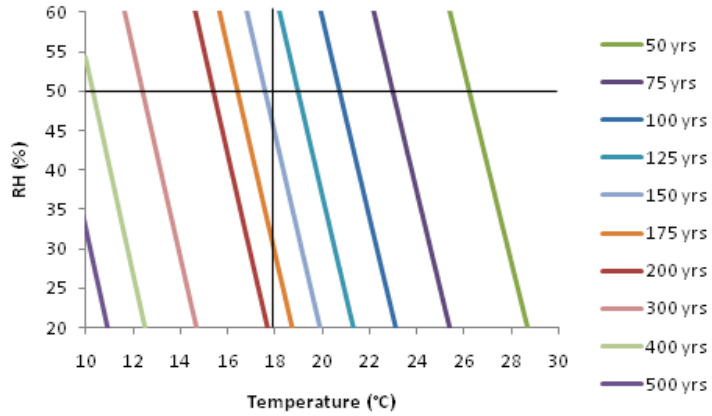
Figure 6.9: RH (%) versus T isoperm diagram showing curves of equal permanence. As in the case of the Sebera [221] isoperms, permanence at 20 ℃ and 50% RH (0 ppb acetic acid) is used to represent a permanence of 1.

However, at this point it would also make sense to include the value-based Unacceptability Threshold calculated in Chapter 5 to the isoperm model. In this manner, points of equal lifetime i.e. points at which the utility value is consumed, can also be calculated and connected into isochrones (Figure 6.10)[6]. Such curves connect points of T and RH combinations with equal lifetimes. It is clear, from these curves, that in the TNA collection the current average repository conditions correspond to an average lifetime of 150 years.

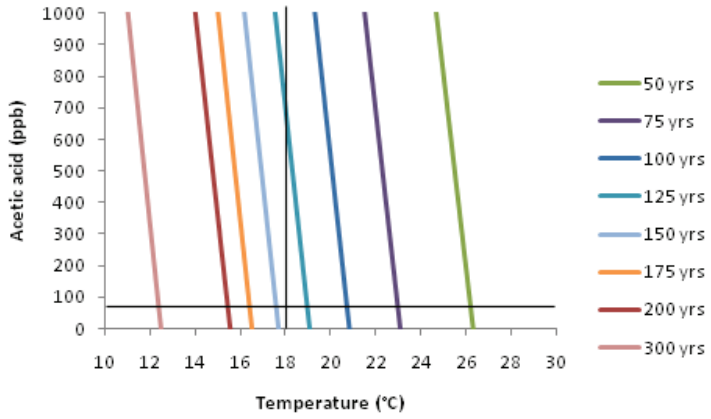
Of course, such curves are not without limits. In this case, the functions were developed with the Arrhenius' equation in mind. Hence, temperatures are being extrapolated on this basis. However, similar cannot be guaranteed for the other parameters, particularly RH.

The functions were built based on data collected at 20-60% RH. As discussed in Chapter 3, gelatine is greatly affected outside of these limits. As these effects were not investigated, it would be unwise to extrapolate these functions far from the conditions investigated. Similar may be said for acetic acid concentration, where even less is known about the effect of greater concentrations. Nevertheless, such conditions of RH and acetic acid concentration are not expected in most archival collections. Therefore, extrapolation to these conditions is not expected to be necessary.

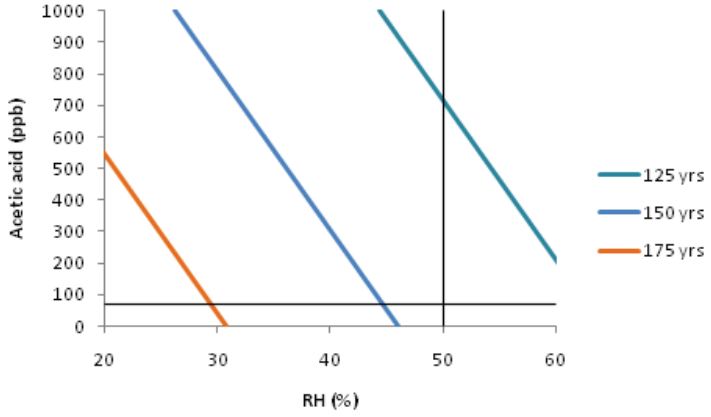
[6]A permanence of 1 was found to correlate with an average lifetime of 111 years.



(a) RH (%) vs temperature (℃) at 70 ppb acetic acid.



(b) Acetic acid (ppb) vs temperature (℃) at 50% RH.



(c) Acetic acid (ppb) vs RH (%) at 18 ℃.

Figure 6.10: Isochrone diagrams showing utility lifetime for paired values of T, RH and acetic acid concentration. Lifetimes are calculated based on time necessary to reach the Unacceptability Threshold, as defined and determined in Chapter 5. The present TNA repository conditions (18 ℃ 50% RH, 70 ppb) are marked on the diagrams.

6.4 Effect of Hypoxia on Chromogenic Prints

Enhancing the lifetime of materials is a major challenge for heritage institutions. As environmental conditions of storage are known to have a significant effect on degradation reactions, modification of the (micro)environment is a potential option to improve object stability [222, 223].

Apart from the options discussed above (control of T, RH and pollutants), removal of oxygen to produce hypoxic or anoxic microenvironments has recently attracted a lot of interest [224, 225]. Oxygen is known to affect chromogenic dye degradation. This has been taken into account by incorporation of antioxidants into layers of the photographic material to control oxygen penetration [17]. However, the effect of low oxygen concentrations on the long-term degradation of chromogenic prints in the dark is not known. Hence, a study was carried out to investigate this.

6.4.1 Methodology

19 sample cut-outs were prepared as for the degradation experiments and placed in 100-mL closed glass reaction vessels with an Ageless RP-3K pack (Long Life for Art, Eichstetten) as a scavenger. The scavenger was changed weekly, and the vial was flushed with dry nitrogen gas. Since the concentration of oxygen was not measured, we cannot assume anoxic (i.e. total absence of oxygen) conditions. Care was taken that the Ageless medium was not in direct contact with the samples. Colorimetric measurements were performed before and after the 4-week experiment, which was carried out at 80 ℃.

A control set was also prepared where no scavenger was added to the vial. The samples for this set were chosen from adjoining areas of identical/similar colour to that used for the samples degraded in hypoxia. After the experiment, ΔE_{T} was measured for all samples as described in the previous chapters.

6.4.2 Results and Discussion

The ratios of ΔE_{T} of a sample exposed to a hypoxic environment, $\Delta E_{\mathrm{T,h}}$ to the colour change of the sample exposed to air (control experiment), $\Delta E_{\mathrm{T,c}}$, are presented in Figure 6.11 for 19 samples of historic colour photographs.

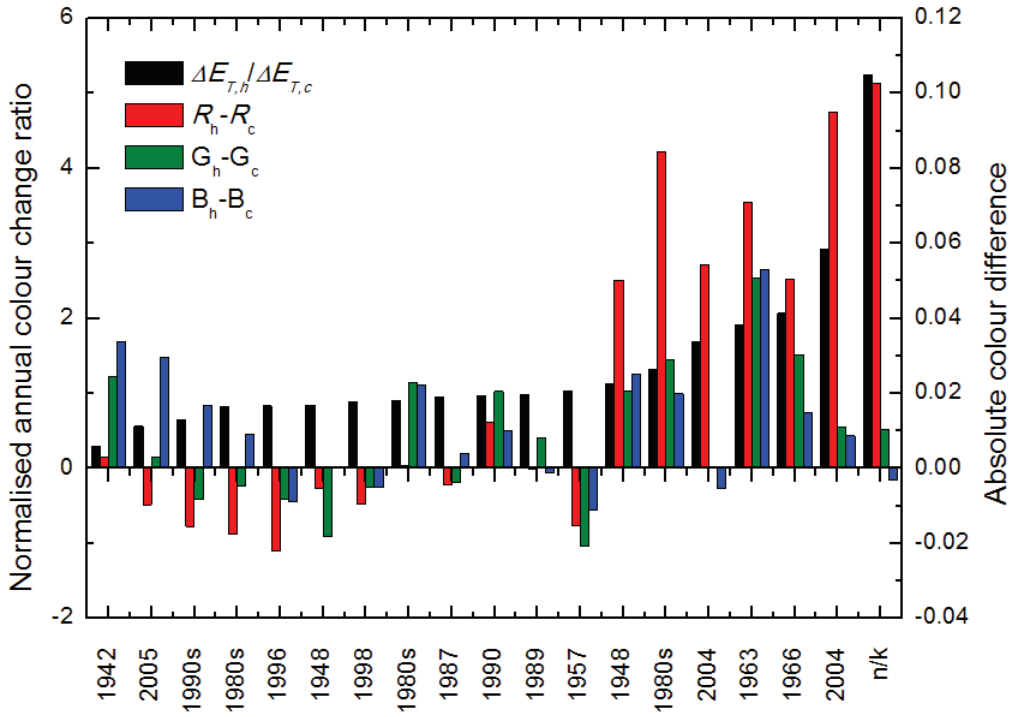


Figure 6.11: Plot of the ratios of normalised colour change between samples exposed to hypoxia, $\Delta E_{\mathrm{T,h}}$, and control samples degraded in air, $\Delta E_{\mathrm{T,c}}$, undergone by 19 colour photographic samples at 80 ℃. Absolute colour differences are presented as difference in R, G and B values, between samples degraded in hypoxia (index h), and control samples degraded in air (index c).

The results of this study indicate that, overall, a hypoxic microenvironment seems to have a positive or neutral effect, with more than 50% benefitting to various extents. However, several samples exhibit lesser stability under hypoxic conditions. This result is not entirely unexpected as dye degradation can proceed via a number of processes, including hydrolysis, reduction or oxidation. The effect of RH on hydrolysis has already been discussed and measured in the previous section, and hence focus in this section fell on the last two processes, reduction and oxidation.

Furthermore, individual dyes in a sample may not all be sensitive to the same agent of degradation. It is known that yellow (complementary to B) and magenta (complementary to G) dyes are often sensitive to oxidation, while cyan dyes (complementary to R) tend to be sensitive to reduction [17, 67]. From the data presented in Figure 6.11, it is evident that in many cases the sensitivity of the cyan dyes is the determining factor: a large positive difference, $\mathrm{R_h}$-$\mathrm{R_c}$, means that the dye de-

graded faster in hypoxia than in the control conditions. This indicates that the dye is sensitive to reductive degradation. In most cases where $\Delta E_{\mathrm{T,h}}/\Delta E_{\mathrm{T,c}} > 1$, i.e. where hypoxia has a negative effect on stability, there is a dominant contribution of differences in the R component of the RGB colour space.

6.5 Conclusion

Accelerated degradation experiments represent a practical way of comparing or predicting the stability of materials under various conditions. By speeding up the reaction rate they provide answers in a relatively short period of time. This is done by increasing the overall energy of a reaction system, typically by increasing the temperature.

The preliminary set of accelerated degradation experiments was carried out to determine the effect of acetic acid, nitrogen dioxide, and formaldehyde on chromogenic prints. It was observed that, on average, acetic acid has the strongest negative effect of the three. Conversely, formaldehyde exhibited a slight protective effect. On the basis of these results, acetic acid was prioritised as the pollutant of critical importance.

The experimental principle used in this investigation was the traditional 'one-at-a-time' experimental design, as usually used in heritage material stability studies. However, such a set-up does not allow factor interactions to be measured. Hence, the CCD DOE set-up was implemented for the investigation of the effects of acetic acid, T, and RH.

Using the DOE approach allowed for a multiparametric dose-response function, taking into account T, RH and acetic acid concentration in the calculation of degradation rate to be developed. The function developed, the fitness of which was throughly tested, is:

$$\ln\left(\frac{\Delta E_{\mathrm{RGB}}}{t}\right) = 32 + 0.0002(\mathrm{AA}) + 0.01(\mathrm{RH}) - 11\left(\frac{1000}{T}\right)$$

where t = time in years; AA = acetic acid concentration in ppb; RH = relative humidity in %; T = temperature in K. Having developed such a dose-response function it was then possible to calculate isoperm diagrams.

By incorporating the Unacceptability Threshold ($\Delta E_{\mathrm{RGB}} = 0.43$), the damage function was also developed and, hence, the average object lifetime can be calculated. The damage function can be expressed as:

$$t = \frac{0.43}{e^{32+0.0002(\mathrm{AA})+0.01(\mathrm{RH})-11\left(\frac{1000}{T}\right)}}$$

where t = time in years until end of lifetime; AA = acetic acid concentration in ppb; RH = relative humidity in %; T = temperature in K.

Useful lifetime of an object has been defined as the period of time until the utility value of the object has been consumed. On this basis, isochrone diagrams can be constructed, linking points of equal lifetime. These diagrams show how changes in one factor can be compensated for by changes in another factor to maintain the same lifetime.

Other factors that might have an effect on lifetime were investigated, namely low-oxygen, or hypoxic, conditions. The conclusion of these experiments is that while hypoxic conditions are beneficial to the stability of most chromogenic prints a significant minority are adversely affected by such conditions. Hence, hypoxia cannot be recommended as a blanket approach for enhancment of lifetime of chromogenic prints.

Having investigated the three lines of research separately, (environmental, material, values) this chapter represents their integration. Experimental design was used for the first time in heritage material degradation studies and based on utility value-based Unacceptability Threshold, the concept of useful lifetime is defined. Isoperms based on the obtained multiparametric dose-response function were calculated and a new plot is proposed linking points of equal lifetime expectancy, the isochrone plot.

Chapter 7

Collection Modelling

Care of photographs should ideally begin at the time a photograph is produced, by ensuring a suitable process of development is followed [58]. However, in an archival context, this level of control is generally not possible. Therefore, collection care is, typically, a process that starts at the point of acquisition of an object by an archival collection.

Collection care may be considered to encompass preventive and interventive conservation [226]. While interventive conservation often takes place once an object is damaged, the aim of preventive conservation is to slow down the rate of deterioration [226].

Where possible, preventive conservation is preferable. Therefore, ways of assessing the preservation measures to be taken to enhance the useful life of the objects need to be developed [25]. This is particularly relevant for chromogenic prints because these photographic materials entered heritage collections relatively recently and there is limited understanding of processes ensuring archival survival [80].

Hence, this work focussed on quantitative evaluation of preservation measures for chromogenic prints in a holistic manner. Having looked at the three lines of research individually - environmental conditions of storage (Chapter 3), material change (Chapter 4), and value considerations for end of lifetime determination (Chapter 5) - they have been integrated into a single damage function to facilitate the management of chromogenic prints in mixed archival collections (Chapter 6). This Chapter discusses the practical survey tool developed for examining chromogenic print stability, the result of which was then integrated into a photographic lifetime calculator.

7.1 Non-Destructive Survey Tool

The first step in the management of photographic materials involves understanding what materials are present in the collection [227]. An examination typically takes the form of collection surveys. At TNA, a mapping survey of the whole collection has been carried out to obtain detailed information of the materials present in the collection and how they are distributed. Such information allows for improved longer term planning in relation to the quality of the storage conditions [79]. By gaining a better understanding of the collection, an understanding of the preservation needs of the collection is then possible.

However, besides materials identification, it is also relevant to understand their stability. This is appropriate because, although different prints might visually seem similar, their dyes may be different and, hence, their stability may differ. Moreover, since we are dealing with heritage objects, it is ideal that non-destructive methods are developed for this purpose.

As discussed previously (Chapter 2), constant changes have been introduced to chromogenic photographic prints to improve properties including stability, colour balance and ease of development. Some of the changes have been major, such as the introduction of resin-coated supports in the 1960s [31, 35–37]. However, since the turn of the century, most changes made to gelatine silver prints have been less obvious such as changes in additives, fillers and optical brighteners.

This suggests that material lifetime could potentially be related and, therefore, modelled, on the basis of changes in material composition. Quantification of these changes and their correlation with material durability is, however, required. The applicability of near infrared (NIR) spectroscopy to dating chromogenic prints has already been discussed in Chapter 4. Hence, this same technique was further investigated for predicting chromogenic print stability.

7.1.1 Methodology

7.1.1.1 Stability Data

The data set of $|\Delta E_T|$ obtained at 80 ℃, 60% RH and 0 ppb acetic acid, as discussed in Chapter 6, were used for this analysis.

7.1.1.2 NIR/MVA Analysis

For the prediction of dye stability, NIR reflectance spectra were measured using a LabSpec 5000 spectrometer (Analytical Spectral Devices) with three separate holographic diffraction gratings and three separate detectors; 512-element silicon photo-diode array for the spectral region 350-1000 nm, and two thermoelectric-cooled indium gallium arsenide semiconductors for spectral regions 1000-1800 nm and 1800-2500 nm. The spectra were measured with an accessory that allowed for collection of spectra in the 45°/45° geometry (spot diameter ca. 2 mm) using a 1-m fibre-optics jumper cable to interface with the LabSpec instrument. This illumination geometry was selected for this particular application in order to collect as much spectral information from the surface as possible.

The spectra were measured over the range 350-2500 nm using 150 scans from the back of photographs as this was the layer that changed the most regularly. The spectra were subsequently manipulated with GRAMS 9.0 software (Thermo Scientific). A Partial Least Squares (PLS) model was optimised using various spectral pre-treatments and the best model was selected on the basis of a comparison of Root Mean Square Error of Cross-Validation (RMSECV) values.

7.1.2 Results and Discussion

7.1.2.1 Analysis of Stability Data

As producers strived to improve the performance of photographic materials with time, it was expected that a correlation might be achieved between NIR spectra and the stability of the prints. Therefore, to investigate image stability, chromogenic prints covering the whole period of colour photography since the 1940s, were subjected to accelerated degradation at 60% RH and 80 ℃, as described in Section 6.3. A wide range of samples was chosen since little is known about their material composition, and only a large enough sample set might reveal patterns of image stability evolving with time or according to producer. Principal component analysis was carried out using the two most represented producers in the sample collection (Kodak and Agfa - 61 samples altogether) and the year of development (1978-2006) to investigate the presence of such patterns.

As evident from Figure 7.1, showing the loading plot obtained using principal component analysis, (in)stability is not associated with either producer as the load-

ing factor for $|\Delta E_T|$ is positioned at almost exactly 90° relative to loading factors for the two producers. This is possibly a result of the two major producers keeping up with each other's technical advances. There is, also, only a minor correlation between (in)stability and year of development. Therefore, none of these parameters can be used even to broadly classify materials in terms of stability.

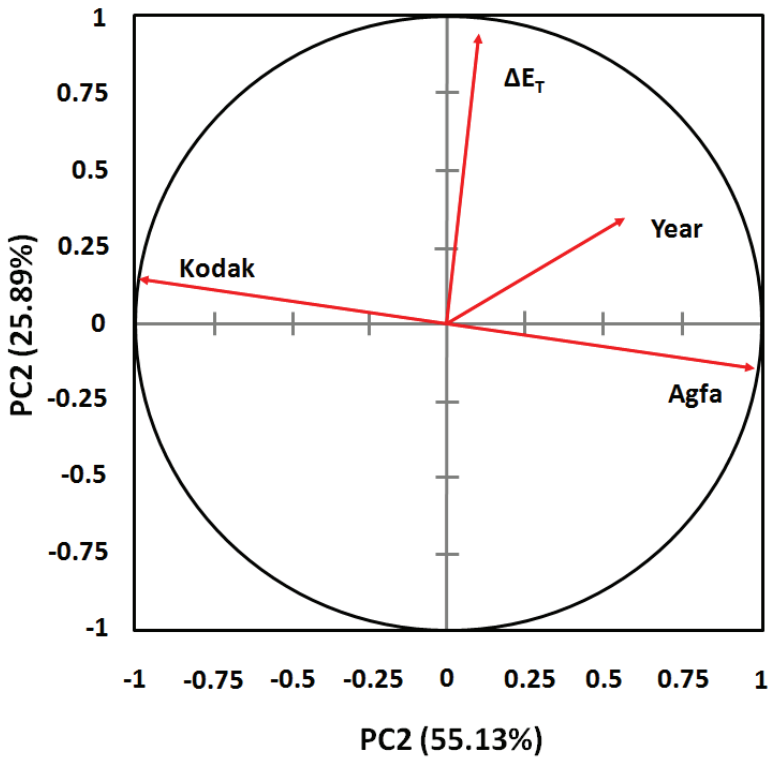


Figure 7.1: Principal component analysis loading plot for image stability ($|\Delta E_T|$) at 80 °C and 60% RH, year of development of the photo and two producers, Agfa and Kodak.

7.1.2.2 Predicting Stability using NIR/MVA

As discussed in Section 4.2, NIR spectroscopy, in combination with multivariate analysis (MVA), is a strong contender as an easy-to-use technique for non-destructive characterisation of chromogenic prints. Therefore, in this part of the study, the ability of NIR/MVA to analyse complex data, was used to develop a tool for predicting the stability of chromogenic prints in terms of the rate of change [17]. Stability data, as discussed in the previous section and obtained using accelerated degradation at

60% RH and 80 ℃, was used in the following analysis. This data set was used as the conditions provided the greatest rate of change and, hence, was expected to have a lower experimental noise to signal ratio. Furthermore, as the multiparametric damage function was built to incorporate such conditions, extrapolation to room temperature was considered to be acceptable.

To develop PLS methods, the region 1700-2425 nm was found to be the most useful. The pre-treatments carried out were Savitzky-Golay 5-point 1^{st} order derivative smoothing combined with a standard normal variate pathlength correction. The correlation between modelled and measured data achieved in this instance (Table 7.1) is not as good as the one obtained for dating (Table 4.4). However, this was to be expected since the stability prediction model is probably based on establishing a link between changes in the support material (giving rise to most of the NIR information) and changes in dye stability (which possibly feature to only a minor extent in NIR spectra due to signal dilution). Furthermore, in this instance, model choice was based on RMSECV as RMSEP could not be determined due to the smaller sample size available. Although the model might not be appropriate as an analytical tool for prediction of the stability of individual photographs, it could be satisfactory for development of a stability categorisation tool for chromogenic prints within a collection (Figure 7.2).

Table 7.1: PLS cross-validation and prediction model data for determination of colour photographic image stability.

		Cross-Validation	
Measured property	Range	RMSECV	R
$\lvert\Delta E_T\rvert$	-4.3-5.3	1.4 $\lvert\Delta E_T\rvert$	0.69

7.2 Photographic Lifetime Calculator

Preservation is a priority of most heritage institutions. However, it coexists with other, sometimes antagonistic, priorities, such as access to the collection. In terms of preservation, in order to balance requirements of different priorities, it is useful to be able to quantitatively compare the effects of various preservation options.

Such assessments of outcomes are typically carried out using modelling. So far a number of tools have been developed for modelling changes to a collection as a

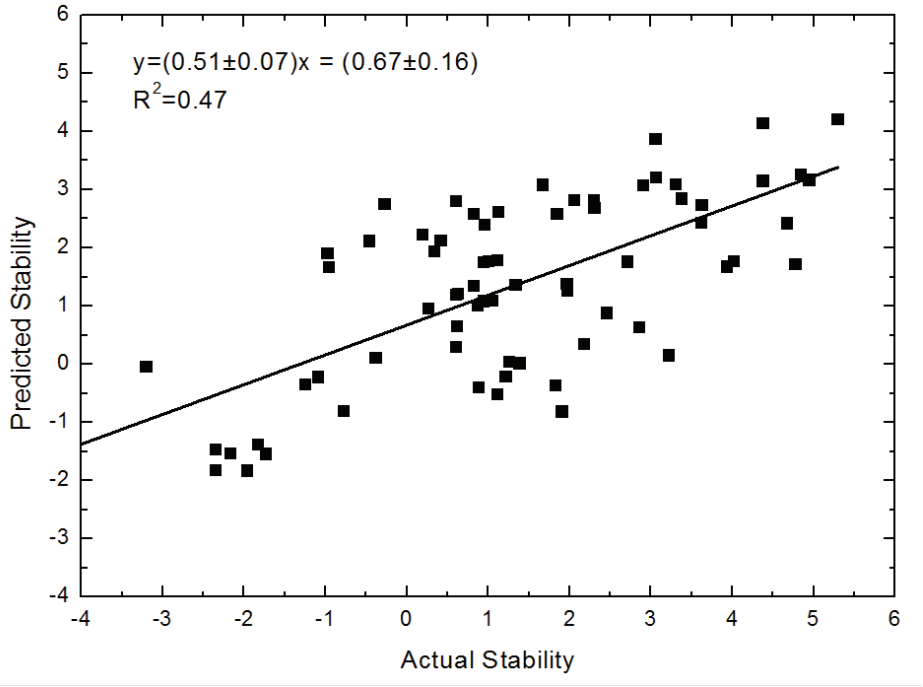


Figure 7.2: PLS cross validation model for the prediction of (in)stability of chromogenic colour prints, measured as $|\Delta E_T|$.

consequence of various preservation scenarios. The most commonly used tools are those modelling risk as well as those modelling environmental effects.

One of the most well known risk assessment methodologies is Waller's model [196]. This methodology identifies the levels of risk depending on frequency and severity and the magnitude of risk is calculated on a per century basis. However, this model is not aimed to provide an understanding of how possible environmental scenarios would affect the objects in a collection. Instead, such information is a prerequisite for using risk modelling. Therefore, it relies on pre-existing data and experience [10] that is not always available but that can be provided by work such as this project.

In this work, the main risks to chromogenic prints in mixed archival collections were assessed and identified as the conditions of T, RH and acetic acid concentration. The aim of this work was not to identify and quantify all the possible risks to a collection, but to identify and explore the risks of environmental degradation. A more comprehensive assessment of risks to TNA's collection using Waller's approach can be found in Bülow [10].

Environmental scenarios are typically investigated using models based on general (i.e. not material-specific) dose-response functions taking into account T and RH, such as the Climate Notebook® by the Image Permanence Institute. This tool provides users with a preservation index (PI)[1] of an environment. However, it does not take into account concepts of changes in value with respect to preservation as it is designed so that 20 ℃ and 45% RH results in a PI of 50 years and other PIs are taken in relation to this [228]. In the case of chromogenic prints, perhaps the most serious disadvantage of this model is that the particular modes of degradation are not taken into account as the Climate Notebook® only considers vulnerable organic materials as a whole. This is an issue with most similar tools in general use in heritage institutions.

The only tool that specifically targets chromogenic prints is the wheel accompanying the IPI's Storage Guide for Colour Photographic Materials [3]. The data for this tool was built on the basis of only four photographic products, and end of lifetime was determined as the point in time where there is a 30% loss of dye density. This tool, however, only models the effects of T and RH. Furthermore, having been built using traditional one-factor-at-a-time accelerated degradation experiments, it does not seem to take into account interactions between degradation factors.

It has, thus, become clear that in order to model a collection of colour photographs, not only would a larger sample set need to be studied, but also models used in other research domains have to be investigated. In particular, stock modelling, well established in management of farmed animal populations (e.g. fish stocks), amongst others, was found to be appropriate[2]. Stock assessment is carried out to understand the status of a stock, and stock modelling to understand the possible outcomes of different management alternatives [230]. It is, therefore, carried out to provide advice on the optimum utilisation of the stock [231].

A basic description of a stock model is that it contains an input and an output that are joined by processes, where the input is a stock rather than an individual item

[1]The PI expresses the effect of environmental conditions of an environment on the decay rate of organic materials, and gives an idea of how long it would take for objects to reach a "state of significant deterioration" [228].

[2]In the context of fisheries science, stocks are a subgroup of a species in a defined geographical area, where intrinsic parameters, such as growth and recruitment, are the only significant factors in determining population dynamics, as opposed to extrinsic factors such as immigration and emigration [229]. In effect, this refers to managed units of a population. In a similar way, chromogenic prints in an archive can be thought of as a managed population, as recruitment is controlled at the accessioning stage.

[231]. In a similar way, the aim of this project was to link environmental and material conditions of chromogenic prints in an archival collection with outputs of lifetime of the same collection. Therefore, stock modelling was identified as an appropriate modelling concept for this project. It is also worth noting that concepts of stocks and stock modelling are widely used in the management of various resources, including building stocks [232, 233].

Once the modelling principle had been identified, the approach to building the model had to be determined. There are two major approaches to modelling, including stock modelling: a top-down approach, or a bottom-up approach.

Bottom-up methods are built up from data on a hierarchy of disaggregated components, that are then combined according to some estimate for their individual impact [233]. In the heritage field bottom-up approaches are employed in various instances, including in engagement of communities in participatory research [234–236]. An issue with the bottom up approach is that it often necessitates extensive data gathering and inevitably results in significant gaps in the data when broad answers are the target, although with the development of data intensive methods and the ubiquity of available data this approach is becoming more common [237].

On the other hand, the top-down modelling approach works at an aggregated level, giving a broad impact picture in a relatively straightforward way [233, 237]. In the heritage field such approaches are often used when looking at the broad economic impact of heritage on other aspects e.g. tourism [237, 238].

In this project the interest was in the way collections, hence stocks, as a whole are affected by environmental conditions, rather than individual objects. Therefore, a stock-modelling approach was considered to be appropriate. A top-down approach was taken to obtain a broad-impact picture. This follows from the aims of the project to understand how a collection as a whole would be affected by various environmental conditions. Furthermore, this approach allows one to identify whether a collection is particularly susceptible to degradation or not.

The final outcome of the modelling experiment is an options appraisal tool for archival managers. The tool allows managers to understand how specific changes to the environmental protocol could affect the lifetime of the collection of chromogenic prints within their archive.

7.2.1 Methodology

Modelling described in this section brought together the outcomes of the previous tasks in the project into one coherent system. Calculations were done in MS Office Excel 2007, split over 3 worksheets. The first worksheet, labelled 'environmental parameters', is where the investigated environmental conditions are inputted by the user and where the output is presented[3]. The second worksheet, labelled collection data, is where stability data is entered (if available). The third worksheet, labelled 'change function', is the back-end of the tool, where calculations are carried out.

7.2.1.1 Input

This modelling component provides the scope for two types of input. The first is an input from a survey of chromogenic prints in a collection using the NIR tool discussed in Section 7.1. This describes the current state of the stock. It is also possible for the user to input the T, RH and acetic acid concentration parameters to be investigated. Therefore, the user has the capability of influencing the outcome based on the collection of interest as well as on the investigated environmental conditions.

7.2.1.2 Process

Based on the stability tool output, the photographic lifetime calculator calculates the relative stability of the photographs in the stock collection[4] to the project collection[5]. It then calculates the lifetime of the project collection at the environmental conditions of interest using the multiparametric damage function developed in Section 6.3. The lifetime of the stock collection is then calculated based on the relative stability of the stock collection items to the project collection.

7.2.1.3 Photographic Lifetime Modelling Tool

The main output is a graph showing the percentage of the stock collection that have reached UT (Figure 7.3). The output shows the lifetime (in years) on the x-axis and the % of the stock collection that has not gone beyond UT on the y-axis.

[3]This is based on a similar model developed for building stock by Dr Mark Barrett (UCL Energy Institute).

[4]The stock collection refers to the collection inputted in the 'collection data' worksheet.

[5]The project collection refers to the collection used in this project to build the model.

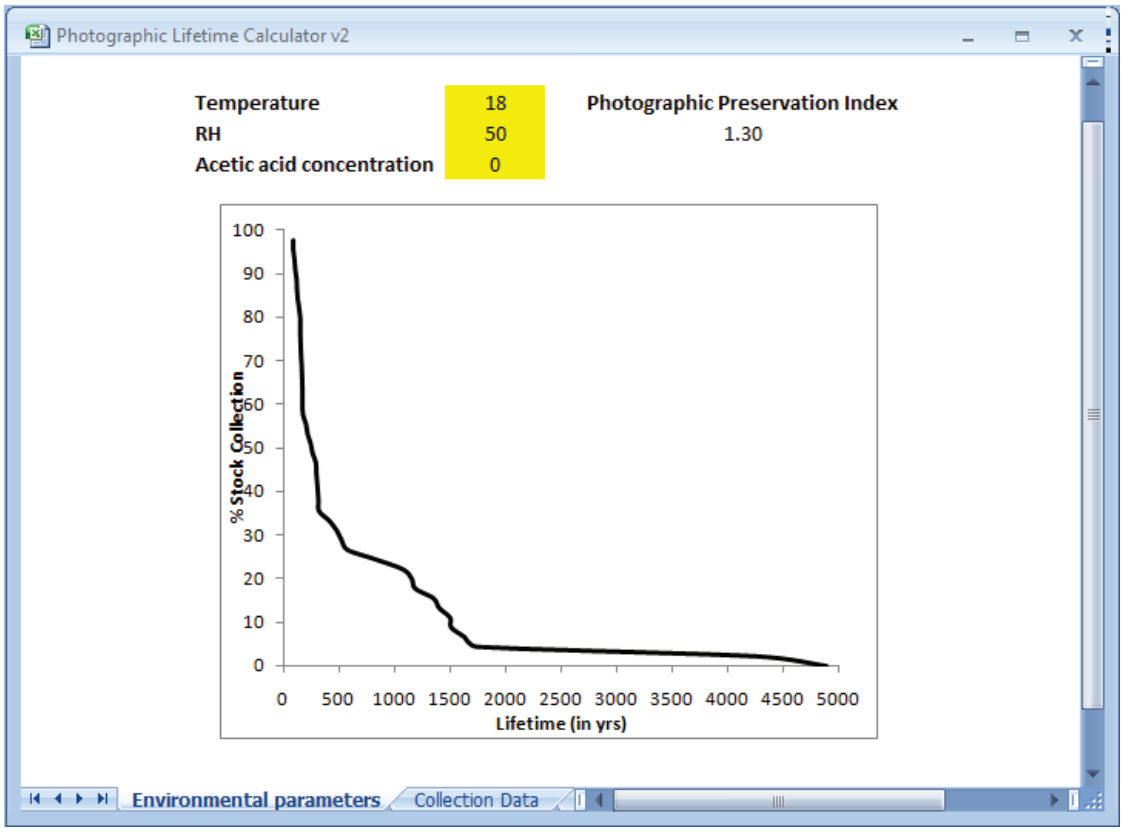


Figure 7.3: Figure showing the environmental parameter input screen and the graphical output showing the lifetime (in years) on the x-axis and the % of the stock collection that has not gone beyond UT on the y-axis. The Photographic Preservation Index (PPI) of the space is also given compared to 20 ℃ and 50% RH. The collection data sheet can be accessed from the sheet tab bars at the bottom left hand side of the window.

The Photographic Preservation Index (PPI) of the space is also given compared to 20 ℃ and 50% RH, as was used to represent a permanence of 1 in Sebera [221].

7.2.2 Results and Discussion

The ultimate aim of this project was to develop a collection modelling tool for more efficient management of chromogenic colour prints in mixed archival collections. In this section the two remaining objectives are investigated:

- To integrate the multiparametric damage function into a photographic lifetime calculator to serve as an options appraisal tool for collection managers.

- To survey colour photographs in The National Archives' collection as a means of testing the photographic lifetime calculator.

The first objective was to construct a computational model for lifetime prediction dependent upon environmental parameters. A stock modelling approach was taken due to the similarity between stocks and processes governing their management, and heritage collections. Using the multiparametric dose-response function developed in the previous chapter, it was possible to link collection stability with environmental conditions of storage. Using these inputs, the output required i.e. the lifetime of chromogenic prints within such collections was possible.

7.2.2.1 Case Study: The National Archives

The final objective of the project was to survey chromogenic prints in TNA's collection to then be able to assess a variety of environmental parameter options. Their collection is a typical mixed archival collection where different materials are stored together within the same archival boxes, making it a relevant and representative collection.

Furthermore, although optimal conditions of storage of chromogenic prints have been recommended, due to the antagonistic pressures of access and preservation in cultural heritage institutions, such conditions may not be appropriate from the management point of view due to issues such as cost and ease of access. Hence, compromises need to be made while ensuring that any associated losses in terms of collection lifetime are sustainable. Therefore, it is appropriate to evaluate the effect of various environmental conditions as a way of making a more informed decision on the environmental conditions of storage.

The first requirement was that a survey of part of TNA's collection be carried out. As photographic material represents only 0.7% of all the materials in TNA's collection [79], and of this only a small percentage is colour photographs, a survey of the collection by geographical location within the building was not considered appropriate.

Moreover, it is not well known where colour photographs are located within the collection. The most detailed description is within outputs from a spot check that was carried out by TNA staff to identify where photographs exist within the collection. This survey identified a number of collections within the archive that contain

colour photographs. Based on this, it seemed appropriate to use the results of this spot check as a starting point for the validation of the stock modelling tool and the collections identified in this survey were investigated to identify the most appropriate collection for further investigation. However, for these results to be much more widely applicable to TNA's collection, a much more comprehensive survey of the collection would be necessary.

The collection[6] 'WORK 65'[7] was found to contain a significant number of chromogenic prints: 367 in various boxes, while in other collections, the number of colour photographs was much lower. Also, the prints were on both fibre based and resin-coated supports, on supports from a number of photographic manufacturing companies, and developed from the 1960s to the 1980s. Efforts to identify chromogenic photographs in the collection from earlier decades had not proven successful. Hence the age spread of photographs in the 'WORK 65' collection was considered satisfactory.

One photograph from each piece in this collection containing chromogenic prints was evaluated to provide an idea of the material stabilities within the collection. The pieces contained up to 34 chromogenic prints each. The mode for pieces containing photographs was of 2 photographs per piece. In total, 71 photographs were surveyed and their stability determined using the non-destructive survey tool developed in Section 7.1.

The investigated environmental scenarios were discussed with TNA's conservation research staff. The temperature set points for the photostore (16 ℃) as well as the general repositories (18 ℃) were thought to be of interest, along with 22 ℃ as

[6]TNA's collection is composed of smaller collections that are assigned a letter code (e.g. WORK) and a class number (e.g. 65). The combination of a letter code and class number, e.g. WORK 65, identifies a series. Each series is then divided into piece numbers e.g. WORK 65 is composed of 278 pieces. Each piece consists of items. An archival box generally contains one or more pieces within the same series. Each piece is often contained within an archival folder within the archival boxes. The photographic items in each piece are typically stored within Melinex® (polyester) sleeves, though some photographic items are also found in albums or attached to sheets of paper.

[7]The letter code WORK indicates records of the Office of Works and its successors, relating to the planning, construction and maintenance of royal buildings and parks, and public buildings and structures of many kinds; also the protection and care of ancient monuments. The WORK 65 series contains photographs recording ceremonial occasions, furniture, government gifts, official residences, equipment for museums, galleries and libraries, government uniforms, and furnishings and fittings. The photographs show the range of the Supplies Division's involvement and responsibility in providing furniture, furnishings and equipment to government offices, law courts and official residences [239].

a temperature beyond the regular operational interval. The RH set-points investigated were 50 and 65% at the three temperatures, as well as 35% at 16 ℃, which is representative of the photostore. An acetic acid concentration of 70 ppb was used as input in all cases as this represents the average concentration measured within archival boxes at TNA (Chapter 3).

The environmental scenarios and the corresponding lifetimes (as represented by time to UT) are shown in Table 7.2. As expected on the basis of the dose-response function the higher the temperature and the higher the RH, the shorter is the lifetime of the collection. An important finding, however, is that prints stored in the photostore have a predicted lifetime around 50% longer than those stored in the general repositories. This is relevant as the vast majority of chromogenic prints at TNA are stored in the general repositories.

Table 7.2: Table showing the average collection lifetime for various environmental scenarios. In all cases, an acetic acid concentration of 70 ppb was used, as this is the average concentration measured within the archival boxes. Lifetimes at 0 ppb acetic acid were also calculated. However, changes in acetic acid concentrations did not affect the lifetime significantly *photostore conditions; ** general repository conditions.

T (℃)	RH (%)	Lifetime (yrs)	IPI (yrs) [240]
16	35	350*	
16	50	300	80
16	65	260	
18	50	230**	50
18	65	200	
22	50	140	
22	65	130	

The lifetimes obtained within this study were then compared to the times to significant dye fading obtained using the IPI Storage Guide for colour photographic materials wheel [3]. From the results obtained it is clear that, particularly at the higher RHs, the wheel would indicate a much shorter lifetime than the photographic lifetime calculator. This is significant, considering that the IPI tool does not take into account any pollutant interactions.

However, this comparison must also be interpreted with caution because the wheel does not take into consideration the stability of the particular collection in question, but chromogenic material collections in general. Furthermore, lifetime in

the two approaches is not synonymous as while this study determined the end of lifetime based on psychophysical studies to determine unacceptable change (Chapter 5), the IPI work used time to significant dye fading based on changes in dye density.

Nevertheless, having taken a stock modelling approach, beside average lifetime, further insights into the collection may be obtained by looking at the output shown in Figure 7.3. The results of a Kolmogorov-Smirnov test for normality indicated that the lifetimes of the collection are not normally distributed ($Z = 1.89$, $p < 0.05$). Therefore, although average lifetimes may be used, they are not necessarily the best indication of collection lifetime; in this case the average lifetime could indicate a greater collection lifetime than would be the case in practice.

From the graphical output it is also clear that the collection may be divided into a number of groups on the basis of their lifetime. The first group, that contains around 70% of the prints investigated, has a lifetime below 500 years. However, another group may also be identified at around 1000-2000 years, and another very small but very stable group at the very top of the range.

An attempt was made to try and identify the reason for these stability groups. As was done previously, a principle component analysis was carried out to identify the presence of a relationship between year of development, lifetime, and Kodak and Agfa as the two major manufacturers represented in the stock collection (Figure 7.4). However, as also identified in Figure 7.1, no strong correlation was identified between these parameters and lifetime.

7.3 Conclusion

Preventive conservation is of crucial relevance to collection care. An essential aspect of heritage science is the development of (ideally non-destructive) collection survey tools that can be easily used by practitioners. Having already investigated the strengths of NIR spectroscopy in Chapter 4, this technique was developed into a survey tool for the prediction of stability of chromogenic prints (Section 7.1). The developed application allows for a user to survey collection items rapidly and non-destructively in order to gain an understanding of the stability of chromogenic prints in the collection. The tool is easy to use with minimal training.

The developed Photographic Lifetime Calculator based on a stock model is an options appraisal tool that enables users to predict the lifetime of chromogenic prints

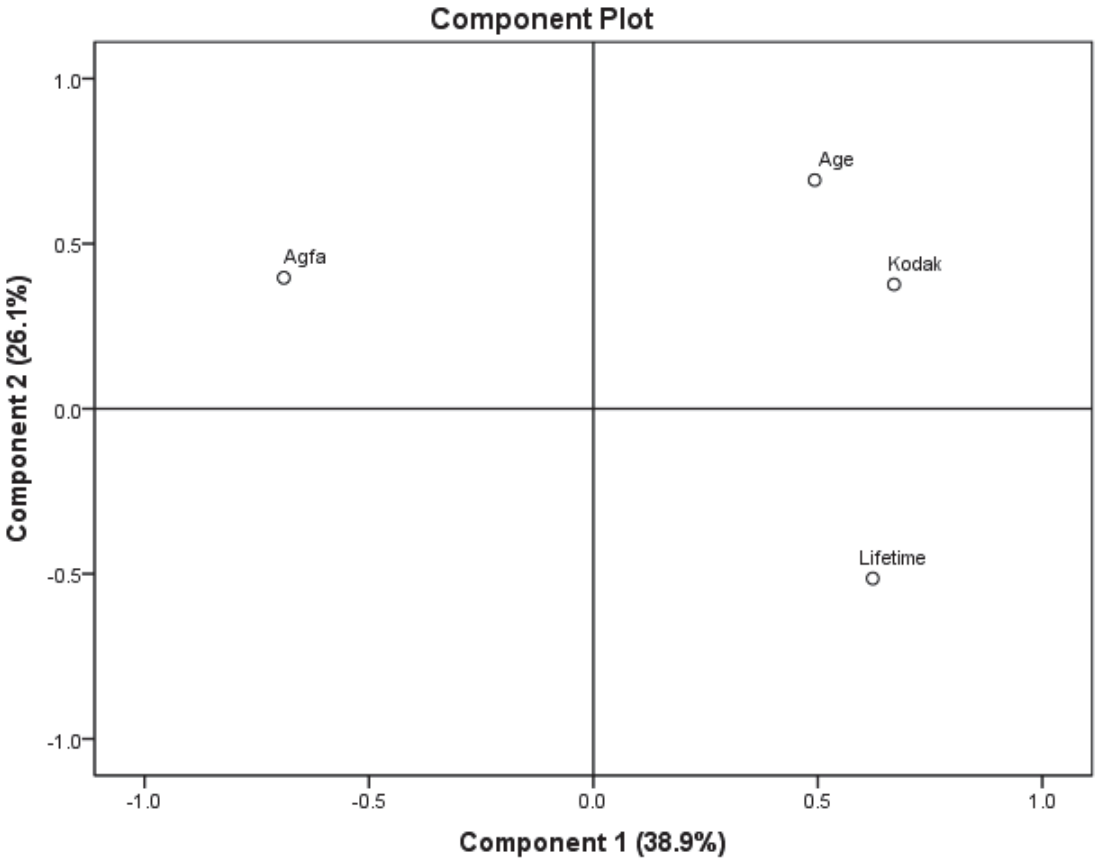


Figure 7.4: Principal component analysis loading plot for lifetime, year of development of the photo and two producers, Agfa and Kodak.

in archival collections under different environmental conditions of storage (Section 7.2). Having developed isoperms and isochrones for paired environmental conditions in the previous chapter, the calculator represents an easy-to-use lifetime calculator that considers the three environmental factors simultaneously. It integrates survey data discussed above with the multiparametric damage function developed in the previously discussed work. TNA's collection was used as a case study showing the capabilities of both the NIR survey tool and the Photographic Lifetime Calculator in assessing the effects of various relevant environmental scenarios on photographic collection lifetime.

Chapter 8

Conclusion and Further Work

This chapter discusses this work's contribution to the theory and practice of preventive conservation. The work's most innovative contributions to heritage science and archival practice are outlined followed by a discussion of the main conclusions arising from this work. Finally, research questions that might be addressed in the future are discussed.

As outlined by Waller [196], in recent years, the field of conservation science has developed from one where answers to specific causes of a problem are sought [241], to one where damage to objects is expressed quantitatively in the form of damage functions relating object susceptibility and environmental parameters to damage [221]. The rigorous analytical approach has been the traditionally taken path to answer these questions.

On the other hand, research related to value has been for very long firmly the remit of arts and humanities researchers, taking a qualitative approach to the question. Such an approach is very difficult to integrate with the quantitative approach typical in the physical sciences.

However, although seemingly disparate, the two disciplines are complementary. The need for interdisciplinary research is strongly felt, as evidenced by the AHRC/EPSRC Science and Heritage Programme, which also provided funding for this work. This work contributes to heritage science by providing a framework for integrating what are often separate lines of research into a single holistic collection model. Such an approach is particularly relevant considering the various antagonistic pressures in the management of cultural heritage collections. The particularly innovative aspects of this work are outlined in the following points:

1. **Degradation studies using experimental design principles.** The traditional approach to understanding the effect of variables on material stability in heritage science has for very long relied on the 'one-factor-at-a-time' method of experimentation. However, such an approach is not as efficient in terms of effort and outcomes as an approach based on design of experiment (DOE) principles.

   This project represents the first study applying DOE principles to the investigation of material stability in the heritage field. This has allowed for the presence of interactions between factors to be measured and integrated into the dose-response function developed. Having shown the appropriateness of such an approach, the methods used in this study may easily be applied to other heritage materials for a more complete understanding of interactions between environmental variables and material stability.

2. **Value and unacceptability of change.** For a long time the word value has been a contentious subject due to its customary reliance and dependence on the individual or group defining it. This has made it a complex concept that is difficult to define. Nevertheless, an unambiguous definition is required in order to define what value is at risk.

   In this work, the institutional priorities of The National Archives were used to define the value of crucial importance, i.e. informational value. Assessment workshops were carried out with stakeholders in order to assess the extent of image degradation considered unacceptable in relation to the information lost. Stakeholders were put in the driving seat in defining unacceptability rather than defining unacceptable change as just noticeable change determined by researchers, which is often the case in similar studies. Such an approach has been identified as a challenge for a number of years [173].

   In this project, the inevitable loss of images due to the inherent instability of dyes was the key issue. The psychophysical approach is hence suggested for similar studies in the future, as it allows for unacceptable change, or damage, to be determined by the stakeholders. To date this has been largely lacking in heritage science research.

3. **Collections and stocks.** Due to its interdisciplinarity, heritage science often finds use for concepts in seemingly unrelated fields of research. The im-

portance of knowledge transfer between different areas of research has been established many times [165, 196]. In this project, correlations were observed between ecosystems and archives: in ecosystems, communities are composed of populations, which are composed of individuals. In archives, collections are composed of groups (populations) of objects of the same material, which are composed of separate items. Furthermore, in an ecosystem, the loss of a single individual does not cause a population to become extinct. Similarly, the value of a collection is not lost if one individual item is lost.

The similarities between ecology and collections led to the usefulness of stock modelling being of use. By thinking of archives as managed populations, concepts of stock modelling used to manage fish populations were applied to the management of archival collections. As a step further, the Collections Demography project recently introduced the use of demographic statistics to management of heritage collections[1].

4. **Isochrones.** Isochrone diagrams show in an intuitive way how changes in one environmental factor can be compensated for by changes in another factor while the lifetime remains constant. To date, isochrone diagrams have not been used in heritage science, mainly due to difficulties with the definition of the end-of-useful-lifetime. While isochrone diagrams are based on the damage function, isoperm diagrams are based on the dose-response function. These are well accepted and have been developed for a number of materials, including silk [242], cellulose acetate [240] and, initially, for paper [221, 243]. Isoperms represent a widely-known tool that archive staff, particularly in conservation departments, are familiar with. The isoperm and isochrone diagrams developed in this project for T, RH and acetic acid concentration enable straightforward appraisal of the three most relevant degradation agents.

5. **Photographic Lifetime Calculator.** In terms of environmental conditions of storage, as seen from isochrone diagrams, an increase in one parameter can be counterbalanced by a decrease in another to provide the same preservation outcome. However, it is difficult to visually represent how more than two

[1] "Collections Demography" On Dynamic Evolution of Populations of Objects, AHRC/EPSRC Science and Heritage Programme interdisciplinary grant.

factors affect photographic collection lifetime using isochrones in a simple and clear manner in 2D.

This computational tool, developed in MS Excel for Windows was, therefore, developed by synthesising the research outcomes of this project. The NIR-based tool developed for predicting stability of a collection was integrated with the multiparametric function developed to provide collection managers with an appraisal tool for assessing environmental scenarios.

8.1 Summary

1. Due to the inherent instability of chromogenic prints, the restricted influence archival institutions have on processing methodologies and limited possibilities for conservation interventions, the factor that is most significant in determining the lifetime of these prints is the environmental conditions of storage. In particular, T, RH and pollutant concentrations were identified as the three environmental conditions of greatest relevance to the stability of these prints.

2. Acetic acid can be considered as the pollutant of crucial importance for two main reasons. First of all, environmental monitoring at TNA showed that acetic acid is the most abundant pollutant in archival boxes; the concentration of acetic acid can exceed that of nitrogen monoxide, the next most concentrated pollutant, by around 10 times (Section 3.3). Secondly, an investigation into the effect of pollutants on chromogenic prints indicated that acetic acid is the pollutant that causes the highest rate of dye degradation in chromogenic prints (Section 6.2).

3. A DOE approach was determined to be the most appropriate methodology for long-term accelerated degradation studies, in comparison with the traditional 'one-factor-at-a-time' approach. It allowed for information on factor interactions to be gathered, in addition to the effect on single factors, while minimising the number of runs (and, hence, resource use) (Section 6.3). This approach allows for the development of multiparametric dose-response functions describing the rate of degradation as a function of several degradation agents (factors).

4. The multiparametric dose-response function developed related the rate of colour change of chromogenic images to T, RH and acetic acid concentration in the following way:

$$\ln\left(\frac{\Delta E_{\mathrm{RGB}}}{t}\right) = 32 + 0.0002(\mathrm{AA}) + 0.01(\mathrm{RH}) - 11\left(\frac{1000}{T}\right)$$

   where t = time in years; AA = acetic acid concentration in ppb; RH = relative humidity in %; T = temperature in K.

5. The 'end-of-lifetime' of chromogenic prints was determined to be significantly affected by image characteristics but not by characteristics of the assessor-group. This was determined using psychophysical categorisation, determining the extent of change considered to be unacceptable for a chromogenic print in an archival context. In particular, the fading profile (selective vs non-selective fading of dyes) was found to significantly affect the outcomes (Section 5.2). Unfortunately, this is not a parameter that can be determined in a straightforward manner for chromogenic prints in a collection. Lifetime was defined as the period of time before which an object becomes unacceptable with respect to its primary value.

$$t = \frac{0.43}{e^{32+0.0002(\mathrm{AA})+0.01(\mathrm{RH})-11\left(\frac{1000}{T}\right)}}$$

   where t = time until end-of-lifetime in years ; AA = acetic acid concentration in ppb; RH = relative humidity in %; T = temperature in K.

6. The regular changes in chromogenic print composition by manufacturers as they strived to improve the product can be exploited using near infrared (NIR) spectroscopy and multivariate analysis to non-destructively characterise chromogenic prints. Two NIR applications were, hence, developed. The first NIR application allows users to date chromogenic prints (Section 4.2). The second application allows for surveying the stability of chromogenic print images (Section 7.1).

7. The use of visible light reflectance spectra was determined to be useful for determining changes in dye concentrations. This is because the chromophoric

systems of chromogenic dyes are optimised to absorb in specific and non-overlapping regions of the visible light spectrum, and the number of dyes is also known to be limited in number in any one object (Section 4.1). In particular, due to the complementarity of cyan, yellow and magenta dyes to red, green and blue, respectively, the sRGB system was determined to be appropriate for monitoring changes in dye concentrations (Section 4.1.2.2).

8. The benefits of hypoxia were found to be dependent on the specific dyes used in a print (Section 6.4). Therefore, although most prints benefited from low oxygen concentrations, a significant number were adversely affected by hypoxia. In particular, cyan dyes were found to be sensitive to low oxygen conditions. For this reason, hypoxia cannot be recommended as a blanket approach for enhancing the stability of chromogenic prints.

9. Storage of chromogenic prints within the photostores at TNA enhances their lifetime by approximately 50% when compared to storage within general repositories in the general repositories.

10. A comparison of the effect of temperature, RH and acetic acid concentration on chromogenic prints showed that temperature has the greatest effect on dye degradation within the limits investigated. Acetic acid was found to significantly affect a number of photographs, though not the collection as a whole.

8.2 Further Work

This work has shown that environmental, material and value lines of research can be successfully combined into a single collection model to better understand the chromogenic prints in the context of mixed archival collections. However, there are various further considerations that can be incorporated into this model to increase its applicability.

1. This project investigated the effect of T, RH and acetic acid, as these were prioritised in the context of mixed archives. In particular, acetic acid was prioritised due to its high concentrations in archival boxes at TNA. However, it needs to be stressed that using the DOE approach, other relevant parameters can be studied, such as light, which could be of interest to stakeholders such

as galleries and museums displaying chromogenic prints. Furthermore, other pollutants might be of interest for chromogenic prints, e.g. ozone and nitrogen dioxide might be more relevant for prints stored in locations that are more exposed to outdoor levels of pollutants, and light to those that are on display.

2. The value element of this project was based on TNA institutional priorities, i.e. a collection where preservation of the information is a priority. However, it must be acknowledged that the value of the objects lies beyond the information they carry. Hence, it would be of interest to investigate the relationships between material change and value changes for other values, such as aesthetic and economic value. It is also worth mentioning that chromogenic prints in collections with other scopes would have different priorities to a government archives. Hence, further research could be undertaken to define the colour change considered unacceptable for prints in other value contexts, for incorporation into the model.

3. In this project it was assumed that the prints were continuously in storage and that their degradation is not affected by use. Therefore, the impact of physical handling on the prints was not investigated. It would be interesting to assess the effects of use on chromogenic prints, including physical properties, as these are expected to be more affected by handling than by storage.

4. An interesting avenue for further research would be to establish whether fluctuations in environmental parameters have an effect on chromogenic print stability, and if so the frequency and magnitude of change that is detrimental to the prints. In this case, apart from concerns for chemical stability it is also recommended to investigate the effects of fluctuations on physical properties.

5. An interesting outcome of the value assessment workshops was that unacceptability was related to the fading profile and the intricacy of detail. It would be of interest to further investigate these two outcomes to determine if these two parameters can be exploited should more directed collection management be appropriate and of interest.

6. Further experimental research is needed to estimate the deposition velocity and absorption capacity of chromogenic prints for different pollutants, and to understand the chemical interactions between the pollutants and the samples.

For such an investigation a dynamic experimental set up that enables continuous flushing of samples with an atmosphere of the required composition would be of interest.

7. It is recommended that further research be undertaken to develop the NIR/MVA tool for stability determination of chromogenic prints as the current tool is not appropriate for analytical use, but rather as a categorisation tool. This can be done by using more sophisticated chemometric methods, such as genetic algorithms.

8. Finally, it is suggested that the experimental approach adopted in this study is applied to other collection materials in future studies. Such studies would allow for a holistic assessment of the impact of various environmental scenarios on various types of collections.

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Appendices

Appendix A

Publications and Conference Papers

A.1 Publications

Fenech A, Strlič M, Krajl Cigić I, Levart A, Gibson LT, de Bruin G, Ntanos K, Kolar J, Cassar M, Volatile Aldehydes in Libraries and Archives, Atmospheric Environment (2010) 44(17): 2067-2073.

Fenech A, Strlič M, Degano I, Cassar M, Stability of Chromogenic Colour Prints in Polluted Indoor Environments, Polymer Degradation and Stability (2010) 95(12): 2481-2485.

Fenech A, Strlič M, Ntanos K, Bell N, Cassar M, Lifetime of Chromogenic Colour Photographs in Mixed Archival Collections, 16th ICOM-CC Triennial Conference Lisbon Preprints, paper 1402.

Fenech A, Strlič M, Cassar M, The Past and the Future of Chromogenic Colour Photographs: Lifetime Modelling Using Near Infrared Spectroscopy & Enhancement Using Hypoxia, Journal of Applied Physics, in press.

Martins A, Daffner LA, Fenech A, Strlič M, McGlinchey C, Non Destructive Dating of Fiber Base Gelatin Silver Prints Using Near Infrared Spectroscopy and Multivariate Analysis, submitted.

A.2 Oral Presentations

Fenech A, Strlič M, Ntanos K, Bell N, Cassar M, Lifetime of Chromogenic Colour Photographs in Mixed Archival Collections, 16th ICOM-CC Triennial Conference Lisbon - Photographic Materials Working Group, Lisbon, September 2011.

Fenech A, Strlič M, Cassar M, Lifetime Modelling of Chromogenic Colour Prints using NIR/MVA, 3^{rd} TechnArt Conference, Berlin, April 2011.

Fenech A, 'Stability of Colour Photographs in Mixed Archives', the Institute of Physics Printing and Graphics Science group Annual Student Conference, Manchester, December 2010. Received Student Presentation Prize in Colour and Graphic Science.

Fenech A, Lifetime of Colour Photographs in Mixed Archival Collections, AHRC/EPSRC Science and Heritage Programme symposium, Oxford, September 2010.

Fenech A, Strlič M, Krajl Cigic I, Levart A, Gibson LT, de Bruin G, Ntanos K, Kolar J, Cassar M, Volatile Aldehydes in Libraries and Archives, 9^{th} Indoor Air Quality Meeting, Chalon-sur-Saône France, April 2010.

Fenech A, Pollution Monitoring at The National Archives, 'Working with Archives' Collaborative Doctoral Students Network meeting, London, January 2010.

Appendix B

Conversion between Colour Spaces

Colorimetric data was obtained in the CIE 1976 L*a*b* colour space. However, for further analysis this was required to be converted to the sRGB colour space. Hence, a colour space converter was built in MATLAB (MathWorks). The source code used is shown below.

B.1 Converting Lab to XYZ

B.1.1 Finding f_x, f_y, f_z

```
fy=(L+16)/116;
fx=(a/500) + fy;
fz=fy-(b/200);
```

B.1.2 Finding x_r, y_r, z_r

```
E=216/24389;
K=24389/27;

if (fx^3)> E;
    xr=fx^3;
elseif (fx^3) <= E;
    xr=((116*fx)-16)/K;
end;

if (fz^3)> E;
    zr=fz^3;
```

```
elseif (fz^3) <= E;
    zr=((116*fz)-16)/K;
end;

if L > K*E;
    yr=((L+16)/116)^3;
elseif L<= K*E;
    yr = L/K;
end;
```

B.1.3 Finding XYZ

```
XYZr=whitepoint('D50');

X=xr*XYZr(1);
Y=yr*XYZr(2);
Z=zr*XYZr(3);

XYZ=[X;Y;Z];
```

This gave XYZ in the nominal range.

B.2 Converting XYZ to sRGB

B.2.1 Finding rgb

The Bradford-adapted, D50 matrix for XYZ to sRGB conversion was used.

```
XYZ_to_rgb = [3.1338561, -1.6168667, -0.4906146; -0.9787684,...
1.9161415, 0.0334540; 0.0719453, -0.2289914, 1.405247];

rgb=[XYZ_to_rgb]*[XYZ];
```

This gave linear RGB.

B.2.2 Finding sRGB

sRGB companding equations were used to convert to the sRGB colour space:

```
if rgb(1)<=0.0031308;
    R=12.92*rgb(1);
elseif rgb(1)>0.0031308;
        R=(1.055*(rgb(1)^(1/2.4)))-0.055;
```

```
end;

if rgb(2)<=0.0031308;
    G=12.92*rgb(2);
elseif rgb(2)>0.0031308;
        G=(1.055*(rgb(2)^(1/2.4)))-0.055;
end;

if rgb(3)<=0.0031308;
    B=12.92*rgb(3);
elseif rgb(3)>0.0031308;
        B=(1.055*(rgb(3)^(1/2.4)))-0.055;
end;

RGB=[R;G;B];
```

Appendix C

The Fitness-for-Purpose Assessment Workshop Materials

Task

On the left hand side there are the set numbers which correspond to the number on the bags containing the colour photographs. In each bag, one of the photographs is labelled 1, and that is the original. The other numbered photographs have then been degraded in different ways. Please classify the photographs in terms of information content within the categorisation scale in the top row.

If you have any questions, please do not hesitate to ask.

How do you evaluate the information content in the degraded colour photographs in comparison to the original?

Set	Favourable	Acceptable	Just Acceptable	Unacceptable	Poor
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					

1. In your daily activities, on a scale of 1 (not at all) to 10 (a lot) how do you rate the following?

		Not at all									A lot
a	When looking at colour photographs, how interested are you in the material?	1	2	3	4	5	6	7	8	9	10
b	When looking at colour photographs, how interested are you in the information contained in the image?	1	2	3	4	5	6	7	8	9	10
c	When looking at colour photographs, how interested are you in the aesthetics of the image?	1	2	3	4	5	6	7	8	9	10

		No knowledge									Excellent
d	How would you rate your knowledge of colour photography (i.e. how it works?)	1	2	3	4	5	6	7	8	9	10

2. How often do you deal with colour photographic prints? (not colour images on a screen or in a magazine)

- Never ☐
- Occasionally (once or twice/month) ☐
- Often but less than 50% of days ☐
- 50% or more of days ☐
- Every day ☐

3. How often do you work with archival materials?

- Never ☐
- Occasionally (once or twice/month) ☐
- Often but less than 50% of days ☐
- 50% or more of days ☐
- Every day ☐

4. Any other comments?

5. In the assessment task today, on a scale of 1 (Not at all) to 10 (A lot) how do you rate the following?

		Not at all									A lot
a	When looking at the colour photographs, how interested were you in the material?	1	2	3	4	5	6	7	8	9	10
b	When looking at the colour photographs, how interested were you in the information contained in the image?	1	2	3	4	5	6	7	8	9	10
c	When looking at the colour photographs, how interested were you in the aesthetics of the image?	1	2	3	4	5	6	7	8	9	10

		Not at all									A Lot
d	Today, how influenced do you feel you were by the type of image e.g. landscape, portrait, technical photo?	1	2	3	4	5	6	7	8	9	10

6. What role do you categorise yourself in with respect to photographs and/or archival/museum environments? (Please select the option you identify with the most)

Conservator	
Scientist	
Collection Manager/Archivist	
Curatorial/Custodial	
Archival User	

7. Any other comments on what were you thinking of when rating the photographs today?